THE

AMERICAN JOURNAL OF PHARMACY.

JANUARY, 1865.

BISMUTHI ET AMMONIÆ CITRAS.

By N. Gray Bartlett.

A preparation, under the somewhat empirical name of "Liquor Bismuthi (Schacht)," was introduced to the profession, some years since, in England, and more recently it has been the subject of several notices in foreign medical publications.

This liquid contains a bismuthic salt in permanent solution, and is miscible with water without precipitation; its reaction is alkaline, and it possesses but little taste. These desirable properties, in a remedy usually administered in a comparatively insoluble condition, would seem to indicate that this solution had not received undue attention.

It is asserted by the originator, Mr. Schacht, apparently after abundant observation, that a fluidrachm of his preparation, containing one grain of teroxide of bismuth, is equivalent, in medicinal value, to a full dose of the subnitrate of bismuth.

The liquor bismuthi was subjected to analysis by Mr. Tichbourne, who found its constituents to be bismuth, citric acid, and ammonia. (Lond. Pharm. Journ., Jan. 1st, 1864.)

Following the directions of that gentleman, for its preparation, recently precipitated teroxide of bismuth was boiled in a solution of citrate of ammonia; repeated trials proved the oxide to be but sparingly dissolved by this treatment, and demonstrated the impracticability of this process. The alternative me-

thod suggested, that of substituting citrate of bismuth for t oxide, yielded a more satisfactory product.

The writer, having observed the solution of citrate of bismut obtained by the addition of ammonia, to have an acid reactio and also that an excess of that alkali occasioned a precipita of oxide of bismuth, inferred the existence of a compound sal of bismuth and ammonia; this was subsequently confirmed.

The following formulas, suggested by theory and numerou experiments, were finally adopted:

Bismuthi Citras.

Take of

Subcarbonate of Bismuth a troyounce;
Citrate of Potassa a troyounce and 120 grains;
Nitric Acid a troyounce and a half;
Distilled water a sufficient quantity.

Dissolve the subcarbonate of bismuth in the nitric acid, and, when effervescence has ceased, dilute the solution with a fluid-ounce and a half of distilled water, gradually added. Dissolve the citrate of potassa in two pints of distilled water, and *to this* liquid add slowly, with constant stirring, the acid solution of bismuth.

Permit the mixture to stand for several hours; then pour it on a moistened paper filter, and, when the liquid has nearly ceased to pass, cover the surface of the precipitate with distilled water.

Repeat this operation until the washings no longer contain nitric acid. Allow the magma to drain, and dry it on bibulous paper, with a gentle heat.

Bismuthi et Ammoniæ Citras.

Take of

Citrate of Bismuth, in powder, a convenient quantity;
Stronger Water of Ammonia,
Distilled Water, each, a sufficient quantity.

Rub the citrate of bismuth with sufficient distilled water to reduce it to a uniform pasty consistence, and add, cautiously, with constant trituration, stronger water of ammonia, until a solution is obtained, observing to avoid an excess of ammonia.

Filter the liquid through paper, returning the first portions that pass, should they be turbid.

Spread the clear solution on glass, that the salt may dry in scales.

Liquor Bismuthi et Ammoniæ Citratis.

Take of

Citrate of Bismuth and Ammonia 260 grains;
Alcohol two fluidounces;
Distilled water fourteen fluidounces;
Water of Ammonia, a sufficient quantity.

Dissolve the citrate of bismuth and ammonia in the distilled water, neutralize the liquid with water of ammonia, and mix it with the alcohol.

Or, take of

Citrate of Bismuth, recently precipitated, and still moist, a convenient quantity;
Water of Ammonia,
Alcohol,
Distilled water, each, a sufficient quantity.

Add gradually to the citrate of bismuth water of ammonia, until the precipitate is dissolved, and a neutral solution is obtained. Dilute this with its volume of distilled water, and filter through paper, returning the first portions of the filtrate, if necessary, until the liquid passes clear.

To half a fluidounce of this solution add hydrosulphate of ammonia in slight excess. Pour the mixture on a tared paper filter, wash the precipitate thoroughly with distilled water, and dry it at a temperature of 212°. Weigh the filter and its contents, deducting the weight of the former to obtain that of the tersulphide of bismuth, which, in grains, is to form the third term in a rule-of-three proportion, thus:

$$(Bi\ S_3)\ \ (Bi\ O_3)$$
$$261 : \ 237 : :$$

the weight of tersulphide of bismuth to that of teroxide of bismuth in half a fluidounce of the solution.

Apply the same ratio to the remainder of the liquid, and dilute it to such an extent that a grain of teroxide of bismuth will be contained in each fluidrachm of the finished solution;

seven-eighths of which measure must be made up with distilled water, and the remainder with alcohol.

For preparing the citrate of bismuth, the subcarbonate is preferable to the subnitrate, because of its more uniform composition, as well as its greater purity, at least in commercial specimens of these salts. The metal itself is inferior to either, as it is almost invariably contaminated with arsenic.

The bismuth and potassa salts are employed in nearly atomic proportions for the production of a neutral citrate of bismuth; the potassa salt, however, is in slight excess on account of its deliquescent nature. By using solutions considerably diluted, the precipitate is rendered less dense, and the washing, by displacement, is thereby facilitated. This is a tedious part of the process, but the best means of accomplishing the purpose. Washing by decantation is inapplicable, for, before it has been carried to a sufficient extent, a portion of the powder will remain suspended in the liquid, and can only be separated by boiling.

It also entails a greater loss of the citrate of bismuth, which is slightly soluble in water. The absence of nitric acid from the washings can be judged of approximately by the taste, but better by faintly tinging a portion of the liquid with sulphate of indigo, and boiling, in a test tube, for a few minutes; if the color be retained, no nitric acid is present.

In the preparation of citrate of bismuth and ammonia, the citrate of bismuth previously dried is employed, in order that a concentrated solution may be obtained without resort to evaporation, as the heat necessary in this operation occasions a precipitate, caused, apparently, by a loss of ammonia.

The solution should be spread with a brush, on panes of glass, to dry.

Citrate of bismuth and ammonia, as thus prepared, is in the form of brilliant white, semi-translucent scales, not at all deliquescent, but readily soluble in distilled water.

An aqueous solution of this salt, if long kept, like those of the citrates in general, is subject to spontaneous change. The addition of small portions of alcohol and ammonia, as indicated in the formulas for a solution of citrate of bismuth and ammonia, will, it is believed, preserve it indefinitely. The same result

could probably be secured by means of sugar, with the additional advantage of a more agreeable taste.

The composition of the compound salt, determined by direct analysis, is as follows:

BiO_3	=	237	=	50·11 per cent.
NH_4O	=	26	=	5·50 " "
$C_{12}H_5O_{11}$	=	165	=	34·88 " "
5HO	=	45	=	9·51 " "
$BiO_3, NH_4O, Ci+5\ HO$	=	473		100.

The bismuth contained in the washings can be recovered by neutralizing them with ammonia, and treating with sulphuretted hydrogen. The precipitated tersulphide of bismuth, after having been washed and dried, may be reduced to the metallic state, or converted into the subcarbonate by suitable means.

The writer is unable to state any facts in relation to the therapeutical properties of citrate of bismuth and ammonia. Owing to its solubility, it would undoubtedly be more perfectly diffused over the mucous surfaces, or more readily absorbed into the system, than the ordinary salts of bismuth.

Accepting the evidence of Mr. Schacht as conclusive, the dose of this salt would be two grains, or of the solution, a fluidrachm.

Chicago, Illinois, November, 1864.

A FLY-LEAF TO MY "ASSAY OF ALKALOIDS."

To the Editor of the American Journal of Pharmacy:

My dear Sir,—The notice which appeared in your last issue of a paper read before the British Pharmaceutical Conference at Bath, by Mr. Thomas B. Groves, of Weymouth, England, as a matter of course requires a few words on my part. When I read it, and before the appearance of the complete paper in the November number of the *Pharmaceutical Journal*, I wrote to you that I did not intend to answer until I should be ready to give the results of my progress within the year past. But the manner and spirit in which that paper is conceived and in which it was received by the meeting at Bath,

obliges me to alter my intention, and to reply beforehand to an attack which is alike unsound and unfair.

The paper of Mr. Groves, it seems, was called out by a self-constituted query of his, "On the Assay of Alkaloids in Pharmaceutical Extracts." In it the author proposes to give a general review of the different processes that have at various times been proposed for the purpose, and to sum up his experience as to which is the best for general adoption. His researches have extended to as many as three modes of conducting an assay, and to two abortive propositions. The three first named are all founded on the precipitation of alkaloids by iodohydrargyrate of potassium, for which I published before all others a systematic procedure in the volume of Transactions of the American Pharmaceutical Association for 1862. Instead of a proposal to substitute something better for this method of mine, Mr. Groves converts by far the greater part of his pages into an effort to bring my statements into discredit, and so far carried away the judgment of his hearers at Bath as to receive permission to print this paper.

First in order, there is a general assertion on the part of Mr. Groves that the iodohydrargyrates of the alkaloids obtained by the reagent, which I directed in 1862, ought to have the formula: Alkaloid + HI + 2HgI, that is, an equivalent of the hydriodate of the alkaloid with two equivalents of iodide of mercury. In consequence, those of my assays in which I employ respectively 1 or 3 or 4 or 6 equivalents of mercury for precipitation are incorrect. Besides, I am charged with having established as a general formula that of: Alkaloid + HI + one HgI.

As I shall investigate Mr. G.'s formulæ at another point, I will here only dispose of this matter so far as my own are concerned. The fact is that, with the exception of the one for opium, I have published detailed assays only for atropia, strychnia, and brucia, and in each of these my results are exactly those required by Groves' formula, viz.: Alkaloid + HI + 2HgI. The two last quoted assays were read before the Baltimore Meeting of the American Pharmaceutical Association in 1863, (Proceed. 1863, p. 251), dated a whole year before my critic's paper, and of the same month in which my assay of opium

appeared in this Journal. I there distinctly compare their composition with that of Hinterberger's double chlorides of the same alkaloids, which probably present the only analogy in that class of compounds. As to atropia, I have never written such a formula as Mr. Groves pretends to copy from me. It is evidently deduced from the formula for morphia of September, 1863, while my assay of atropia was written in December, 1862, and appeared in your January number of 1863.

The truth is, that in the paper last quoted I did not publish any formula whatever; but what Mr. Groves alludes to is a line in the first part treating on alkaloids generally, where I use the following words: "*The compounds formed are the hydriodates of the bases with iodide of mercury.*" I was not indebted to Mr. Groves for this information; it was my own view of their constitution, which was strengthened by that of Boedecker's compound of nicotia. But it would be strange if Mr. Groves could not tell what caused me to give expression to this phrase. Must I recall that in his first paper (published on page 97 of Vol. xi. of the *Journal of the Chemical Society*), his formula was not what it is now, but *alkaloid + sesqui-iodide of mercury*, viz., Alk.+ Hg_2I_3? Well was it then for me to state that they are the *hydriodates* of the bases with iodide of mercury, and I did so at the time, not in the least acquainted with the able manner in which Mr. J. Dyson Perrins had previously handled Mr. Groves' assumptions in the later pages of the *Pharmaceutical Journal*, (Vol. xiii. pp. 241 and 340.)

I come next to a personal matter, which I believe will now be understood in its true light.

My critic attacks my mode of assaying the residual liquid with silver, and (in italics) throws out the suggestion that, in my assay of atropia, I have been guilty of recording a falsehood. I grant that if any chemist, whether personally acquainted with me or not, can be made to believe of me, to what the argument leads, that after stating at the head of the paragraph the exact quantity of reagent required, I could have used *four times* that quantity, and having found that I had done so in one experiment, could have been guilty of doing the same over and over again,—then I stand convicted. Bent upon discovering errors, he reads residuary silver for combined halogens, and,—here is

the laughable side of this incident,—in attempting to bring into discredit my assay of atropia by controverting its results, he entirely overlooks the fact that in so doing he also upsets one of his own formulæ, that of atropia + HI + 2HgI. I have never used any other for it.

In my original paper I recommended measuring in the liquid portion of the mixture holding the precipitate, the excess of iodine and chlorine by a solution of silver, and without filtering. The latter is quite practicable in the case of atropia and some bases where the precipitates form a resinous mass, but is not generally applicable, and was withdrawn by me in my paper on opium. Mr. Groves falls foul of this non-filtration, but admits that there are a few exceptions in which it may be done, and that I had myself directed filtration; yet he omits to state that *atropia is one of his cases of exception.*

Something, I am sure, altogether unheard of in reviewing a method in chemistry, and especially a volumetric process, is that the critic does not in the least pretend to work with the same solutions as the original author, but uses liquids of a degree of dilution which he imagines better adapted for the purpose. Now, whether this be so or not, there are certain alkaloids which show variations according to dilution similar to those produced in Bunsen's iodine-assay, according to whether different solutions of sulphurous acid are employed. My equivalents of iodohydrargyrate are all taken with a tenth normal liquid against one percentum of alkaloid in solution. I also gave a grain or troy-test liquid of one-fifth the strength of my metrical solution. But in the paper on opium I stated that owing to the solubility of the precipitate with morphia, the former troy-liquid was too weak to give accurate results, and that one of five times the strength was to be used, that is, of the same strength as the metrical solution. For the assay of strychnia and brucia, however, I retained the original weak solution as sufficiently accurate for pharmaceutical purposes.

My solutions of alkaloid contain either one-half or one per cent., at least, in those cases where I have published detailed researches. In these I never use less than 10 cubic centimeters, about 225 drops, but in most cases 20, 30, or 40 c. c., repeatedly and in succession.

Mr. Groves' alkaloids vary with the equivalent between one, and four-*tenths* of one per cent., and the quantities with which he has compared and by which he would subvert my numbers are one hundred grains of these liquids, a large sized teaspoonful. These, morphia and all others, he compares with a test liquor of exactly the strength of my original (1-5th) troy solution.

As a consequence, wherever I have prescribed dilute solutions in both cases, as less than one-half per centum of strychnia, and allow, as in this instance, the weak mercuric solution, the numbers agree well enough to receive Mr. Groves' approbation. But mark the difference in the case of morphia:

	Of his test liquor,
Mr. Groves supposes, according to his theory, that he requires	100 grains.
He actually requires	70 "
Reduced to his numbers, my metrical solution is consumed to the extent of	75¾ "
Reduced to his numbers, my strong troy solution with Groves' solution of morphia is consumed to the extent of	78 "
My theory requires	75 "

The strength of the solution of morphia, I have stated in my assay of opium, should be such that after precipitation with the reagent the whole bulk of precipitate and liquid when diluted for filtering and testing with silver may represent not less than 0·3 gramme of morphia in 100 c. c.; that is, 1 c.c. is equal to the filtrate from 0·003 gramme of morphia after precipitation; the space of 0·3 c. c., supposed to be occupied in the 100 c.c. by the dry precipitate, is not counted. This is almost precisely the dilution of Mr. Groves' original solution (=0·303 grain in 100). The difference between the two modes of assaying then is, that he measures a dilute solution with a test liquor of one-fifth the strength of mine, while I have assayed with mercury a more concentrated solution (1 p. c.), and after reducing the liquid to the strength of the original one of Mr. Groves, measure it again with silver. If any cause for error may arise, dilution for instance, it is existing in his solution from the beginning, in mine only after removal of the precipitate; and while the former is constantly growing weaker by the addition of test-

liquor, by filtering and washing,—the latter, together with all test-liquids and washings added, only reaches the strength of Groves' original solution at the last.

He does not perceive this, but impresses upon his hearers the belief that I continue to dilute the liquid indefinitely. "But when strong solutions are used the precipitate is either clotty or gelatinous, and not to be washed without much water, thus reproducing the difficulty sought to be avoided."

Mr. Groves' logical conclusions sometimes differ from mine, as in this paragraph on morphia.

His theory requires that equal parts of both liquids should be consumed, but his reaction stops at 70, not at 100. Hydrosulphate of ammonia indicates mercury in solution, and after (or before?) adding more iodohydrargyrate, strychnia likewise gives a precipitate. Hence he concludes that there is already an excess of iodohydrargyrate. So that out of 70 parts of test-liquor, which contain about one and a half equivalents of mercury, he has actually extracted his two equivalents and over. He is bound to contradict the evidence of his senses, because they seem to confirm my view; nor does he stop to inquire and to decide by the simplest test possible what causes the precipitate to re-dissolve. His "series of experiments showed the cause of this to be the ready solubility of iodohydrargyrate of morphia in iodide of potassium. It is also soluble in *hot* water." I stated more than a year ago that this compound of morphia was unusually soluble in water, meaning, of course, water of the ordinary temperature, and was therefore not surprised that *on evaporating the filtrate to one-third, the whole of the precipitate held in solution separated in perfect order.* Would it have separated if the iodide of potassium had been its solvent?

There remains, in fact, no doubt but that my original proportion of 3 mercury to 2 morphia correctly expresses the proportion of test-liquor required for this alkaloid. And no experiments of mine have as yet been able to induce me to depart from the proportion in which I have combined the ingredients, and thus to destroy the uniformity of the method.

As here, so elsewhere, the composition and quantity of the precipitate are not always expressed by the equivalents of test-

liquid for a given quantity of alkaloid, but by a definite fraction of that equivalent.

As proof of this I will give some analyses by other chemists, while the main question shall be proved by Mr. Groves' testimony.

Bœdecker (*Ann. Chem. Pharm.* lxxiii. p. 372; *Gmelin*, vol. xiv. 228) describes a compound of iodide of mercury with hydriodate of nicotia of the formula, $\dot{N}ic$, 2HI+2HgI. This is the composition of the precipitate formed by *four* equivalents of mercury, but crystallized from excess of hydriodic acid.

Wertheim (*Journal f. pr. Chem.* vol. 91, p. 481—*Chem. Centralblatt*, 1864, p. 791), gives the preparation of another iodohydrargyrate of nicotia of the formula—$\dot{N}ic$+HI+2HgI, obtained by boiling an alcoholic solution of $\dot{N}ic$ HI, with a large excess of mercuric *oxyd*. The same chemist, in the same paper, describes a third compound, without hydriodic acid, produced by treating a mixture of mercuric iodide in nicotia with boiling water; this has a composition according to $\dot{N}ic$+2 HgI.

Which of these formulæ has Mr. Groves found by analysis? He unhesitatingly adopts the second, while in his volumetric assay he had to use almost exactly the quantity of mercury which my assay requires, i. e., four equivalents. What then has become of the two equivalents of mercury?

Now, one of the very first points upon which Mr. Groves differs with me is this excess of mercury in solution, of which, in my paper of December 10th, 1862, I spoke in the main as follows: "In the reactions between some of the alkaloids and the iodohydrargyrate of potassium (the solution of one HgCl in 3KI) the mercury partly remains in solution. For this reason not a solution of iodide of mercury must be used, inasmuch as with a solution of the latter the results very much differ; nor must the solution of alkaloid be added to the mercuric solution, but the latter to the former." This, I presume, shows that even then I was aware of several causes of ambiguity, and that in order to secure uniformity in the results, I desired to use but one test liquid and one mode of proceeding.

Mr. Groves, on the other hand, concludes that my mode of

assaying alkaloids cannot be correct because of this statement. As support for this belief of his, he gives no experiment nor proof whatever, but his individual opinion, that "he could not see any reason why any mercury should necessarily remain in solution unless an excess of iodohydrargyrate had been added, or the resulting alkaline compound was to some extent soluble, (meaning as such)." "Whether," he continues, "we have compounds of one equivalent of Alk. HI, and one or more eq. of HgI, an equation can be formed to meet the case, leaving no uncombined mercury in solution."

For the purpose of proving this against him it is necessary to introduce the record of his assay with quinia and cinchonia.

I. *Quinia* requires, according to

Mr. Groves' theory.	His results show,	My results are,	My theory requires.
$\overset{+}{Chi}+HI+2HgI$			$2\overset{+}{Chi}+3HI+6HgI$
100.	140 and over.	148 to 151.	150 grains.

His experiments, it seems, were made at night, at the seasonable hour of 9 P. M. "After 130 grain measures had been added the filtrate reacted still with iodohydrargyrate, (N. B., because there was still some quinia in solution), but not with quinia, (N. B., because there was not then any mercury in excess); but with 140 it reacted decidedly with both reagents; at 9.30 P. M., half an hour after, the same liquid reacted decidedly with quinia, but scarcely perceptibly with iodohydrargyrate." This last deportment is what proved a stumbling block to Mr. Groves' perception, and he concludes not only that my numbers are incorrect, but also that the alkaloid-compound itself passes into solution.

My own observation of what passes at the end of this reaction differs, probably because it was made in day-light. The reagent, which in my hands is always five times as strong, when added to the amount of $5\frac{1}{2}$ eq. of mercury produces a canary-colored, flocculent precipitate, which settles very rapidly and leaves a cloudy liquid above it; when this is now filtered on a watch-glass, every drop of fresh test liquor will produce a white, crystalline precipitate, which continues exactly up to the point of saturation, i. e., of 6 equivalents of mercury. This is still better observed at the end in the glass vessel containing the

whole mixture. If, after the reaction on the watch-glass becomes indistinct, the glass beaker is shaken for one minute, the mixture will settle almost clear, and upon now adding drop for drop more of the reagent, it sinks to the bottom and at once forms a dense cloud over the stratum of precipitate, if any quinia be left in solution. Whenever the cloud no longer makes its appearance, the numbers consumed, with the usual deduction for surplus, will represent 6 equivalents of mercury. In the meantime the color of the precipitate will have changed to white.

My view of the cause for this retardation is, that 2 eq. of quinia require 6 eq. of mercury for complete precipitation; that when a considerable excess of KI has accumulated, it will tend to re-dissolve a portion of HgI, and destroy the yellow color; and that this is the cause why a fresh solution of quinia or any other alkaloid will then produce a precipitate: while in the dilute mixture the action of the now very much diluted alkaloid on the mercury is overpowered by the solubility of the latter in the great excess of KI; but that when a fresh quantity of mercury is added, held in solution by a small excess of KI only, this will in part rescue the re-dissolved mercury and then act on the remaining alkaloid, similar to a solution of nitrate of silver that will precipitate all the silver from a solution in cyanide of potassium, but is itself involved in the precipitation.

In fact, the filtrate shows the presence of mercury if none whatever is added in excess, but not a trace of quinia. I think nothing remains but to conclude that the mercury in solution will have to be deducted from the formula of the alkaloid-precipitate, which originally was $2\dot{Chi}+3HI+6HgI$, and became $2\dot{Chi}+3HI+5HgI$, or was changed in some similar manner.

How closely my reasoning coincides with what actually occurs is shown by Mr. Groves himself. The formula for the quinia compound, which he published in 1858 and confirms in this paper, is $\dot{Chi}\,HI+2HgI$. As will be seen, the result of his analysis does not agree with the formula; but to admit that the formula was incorrect would upset his theory of the precipitate.

So we have:

Mr. Groves' Formula. $\dot{Chi}+HI+2HgI$.		My Formula. $2\dot{Chi}+3HI+5HgI$.	
Quinia	324	2 quinia	648
HI	128	3 HI	384
2 HgI	454	5 HgI	1135
	906		2167

The formulæ require, in 100 parts,

	Groves' formula.	His analysis.	My formula.
Quinia (+H)	35·88	30·40	30·05
Iodine	42·05	46·52	46·88
Mercury	22·07	23·08	23·07
	100·00	100.00	100·00

This simply means that Mr. Groves' analysis establishes my theory.

It would be wrong to leave the impression as if he entirely approved of his results; but the very singular conclusion that he arrives at is, that all other chemists are mistaken in the matter of the equivalents of the cinchona-alkaloids. He suggests that they be revised, and raises the further question, "whether or not the rectification of equivalents may be extended to other alkaloids less known than the cinchona series." This paragraph I must take for an acknowledgment on his part that there really are other precipitates which do not agree with his theory!

What has been said in regard to the quinia salt refers equally to that of cinchonia. I must here remark that, with a carelessness quite peculiar, in recording experiments, if not in conducting them, he allows us to suppose that 100 grains of the quinia solution in one case required 140, and in another 230 grain measures of test liquid; for, although it must be supposed that in the latter case he used twice the quantity of alkaloid, he never alludes to it, but allows the reader to draw his own conclusions from the glaring discrepancy in the results; and he continues this precisely in the same manner in his assay of cinchonia.

II. Cinchonia.

Mr. Groves' formula $\dot{C}in+HI+2HgI$.		My formula. $2\dot{C}in+3HI+5HgI$.	
Cinchonia	313.	2 Cinchonia	626.
HI	128.	3 HI	384.
2 HgI	454.	5 HgI	1135.
	895.		2145.

In 100 parts:

By his formula.		His analysis.	My formula.
Cinchonia (+H)	35·09.	28·56.	29·47.
Iodine	42·57.	47·45.	47·22.
Mercury	22·34.	23·99.	23·31.
	100·00	100·00	100·00

His assay, altogether owing to dilution, differs from mine as 190 to 156.

I cannot conclude this paper without some words about Mr. Groves' strictures with reference to my method in analysing extracts. As I have never pretended to determine the separate quantity of alkaloids until I had really eliminated them, and since I have never analysed a juice or extract without previously acidulating it, I cannot perceive the drift of some of them. There is one instance in which he apparently contradicts a statement of mine about the precipitation of albumen by my reagent. I said two years ago that the precipitation is not interfered with by the usual constituents of pharmaceutical preparations, except alcohol and acetic acid, and that not even albumen caused a disturbance. I had previously ascertained that a strong solution of this substance remained perfectly clear upon the addition of iodohydrargyrate of potassium, and that its precipitate by corrosive sublimate was redissolved by iodide of potassium. I may now add that under ordinary circumstances no precipitation of albumen is caused by the reagent in watery solutions of extracts, unless they contain a very large excess of mineral acid. All such minute quantities of albumen are likewise precipitated by chloride of mercury, and there is no ob-

jection to their previous removal by this means. The precipitate from iodohydrargyrate at once disappears when the acid is neutralised, that with corrosive sublimate turns yellow with the alkali.

In place of the various proposals for the separation of alkaloids from vegetables and preparations with which we have been favored, I can recommend the process of which I have given an outline in my paper on tobacco, read before the last meeting of the American Pharmaceutical Association at Cincinnati. It is apparently still capable of improvement, but in an assay will answer all the purposes of the delicate method of Stas.

The process is founded on one of Heinrich Rose's suggestions in his paper on the decomposition of iodide of mercury. By adding a clear solution or a mixture of protochloride of tin in caustic alkali to the precipitate, all mercury is at once precipitated in the metallic state, and if the mixture be now shaken with ether, all that is soluble in this menstruum is taken up. When the solution from which the original mercuric precipitate has been obtained was impure and of a dark color, it is better at once to redissolve the alkaline mixture without the ether, in sulphuric acid, and to determine the alkaloid *de novo* in the filtrate. If the alkaloid be insoluble in ether, the alkaline mixture is thickened with bi-carbonate of soda in large excess, and then treated with alcohol; the solution in the latter is freed from iodides by an aqueous and acidulated solution of acetate of lead.

I could have wished that after all this labor I might say that Mr. Groves had left behind in this memorial something which we could consider an addition to our knowledge of the matter he had taken in hand. It is easy enough to tear down or injure a structure; but whoever lends a hand in this, should also be prepared with material for the new building.

As it is, surely my assay has borne no damage from the encounter,—at least I hope that you, Mr. Editor, and your readers, will judge so.

I remain yours truly,

FERDINAND F. MAYER.

College of Pharmacy, New York, December 5th, 1864.

NOTE ON CHLORODYNE.

By Charles Bullock.

[Some time ago the late Dr. Franklin Bache presented us with a blue vial of "chlorodyne as introduced by Dr. J. Collis Browne," &c., &c., "manufactured by J. T. Davenport, 33 Great Russell St., Bloomsbury, London," which had been sent to him. The vial had a glass stopper, and was tied over with skin. Mr. Bullock being engaged in an attempt to produce "chlorodyne" by the recipe published in the *Chemist and Druggist*, Feb. 15th, 1860, the above specimen was submitted to him for comparison with his product. In justice it should be said that the vial had never been opened, but gave indications of not being so tight as to prevent loss of hydrocyanic acid, yet it was too nearly full to admit of much waste of chloroform. The following note from Mr. B. gives the result of his examination.—Ed. Am. Jour. Pharm.]

Philadelphia, Nov. 9, 1864.

Wm. Procter, Jr.:—

I herewith return the bottle of chlorodyne, and am much obliged for the opportunity of inspecting "Davenport's original," as introduced by Dr. J. Collis Browne, Army Medical Staff."

What is chlorodyne? Those who have attempted to put together the supposed ingredients after the instructions of Dr. Ogden, (Vide Am. Jour. Pharm., vol. xxxii..pp. 181 and 334,) have doubtless found that the pharmaceutist "was not at home" when the recipe was devised.

Perchlorate of morphia is almost entirely insoluble in chloroform, and the addition of the other ingredients mentioned in the recipe will not cause the morphia to be retained in solution. The amount of chloroform directed is evidently much in excess of what is contained in Davenport's chlorodyne.

A portion of chlorodyne was agitated with absolute alcohol, and the alcohol decanted from the viscid residue, insoluble in this menstruum.

The alcoholic solution, when mixed with water, occasioned but a faint cloudiness, indicating that oily or resinous substances were present only in minute quantities.

A solution of nitrate of silver, added to the alcohol, rendered it slightly turbid; a few drops of ammonia made the solution clear again. Hydrocyanic acid was thus shown to be absent in this specimen. After dilution with water, carb. of soda did not affect the alcoholic solution.

Another portion of the alcohol was evaporated in a watch-glass; a small portion of viscid matter was left, having a pungent, peppery taste.

The matter insoluble in alcohol appeared to be glucose. It dissolved readily in water. A drop of sulphuric acid was added, and the solution filtered. A few green streaks were left on the filter, resembling chlorophylle. To the solution carbonate of soda was added in slight excess, which caused a flocculent matter to separate; this was collected, and found to re-dissolve readily in water acidulated with acetic acid. A dilute solution of potassa again precipitated it. The precipitate, agitated with an excess of potassa, dissolved but sparingly; the clear solution again afforded a precipitate on being neutralized with acetic acid. This reaction would indicate the presence of morphia, though the appearance of the precipitate, when examined under a glass, was not recognized as the usual form of this alkaloid. That portion insoluble in potassa was again dissolved in dilute acetic acid; to the slightly acid solution carbonate of soda was added in excess. After standing an hour or two the solution remained clear. On heating it sufficiently to expel the free carbonic acid present, the solution became turbid, and deposited a flocculent matter, which, under a glass of 60 diameters, appeared amorphous, was sparingly soluble in spirits of wine, and infusible, charring when heated.

Of the alkaloids from opium, codeia behaves with reagents somewhat similar, viz., not precipitated from weak acid solutions by alkaline carbonates immediately, and not precipitated from its solutions by ammonia. The alkaloids strychnia, brucia, and veratria are soluble in a solution containing free carbonic acid. The absence of the first was indicated by the want of its characteristic bitterness, and the last two by insolubility in alcoholic menstrua.

Having encroached as far on the contents of the bottle as I felt free to do, I have not determined to my own satisfaction the character of the alkaloids present in chlorodyne, and hope that some of the correspondents of this Journal will give us more information concerning this nostrum.

About two-thirds of chlorodyne appears to be treacle; the remaining one-third chloroform, a small amount of water, in

which the alkaloids are previously dissolved, a little peppermint, and capsicum,—and perhaps some cannabis indica.

The following recipe will furnish a preparation having the pharmaceutical properties of chlorodyne, according to Dr. Ogden:

℞

Muriate of morphia,	grs. viii.
Water,	fl. ʒss.
Perchloric acid (25° B.)	gtt. xx.
Chloroform,	fl. ʒjss.
Tinct. of Indian hemp,	fl. ʒj.
Hydrocyanic acid (U.S.P.)	gtt. xii.
Molasses,	fl. ℥ss.
Oil of peppermint,	gtt. ij.
Oleoresin of capsicum,	gtt. i.

To the morphia and water in a small flask add the perchloric acid, and heat until a clear solution is obtained. Then add the molasses, previously warmed to render it fluid. Heat the mixture, and agitate well. When cold, add the other ingredients, and mix thoroughly.

MANUFACTURE OF PERCHLORIC ACID.

By Charles Bullock.

Having occasion to prepare perchloric acid in some quantity, the process of M. Deville for obtaining fluosilicic acid was tried as a preliminary step.

The process of M. Deville consists in passing steam through a mixture of fluorspar and silica heated to redness. The water is decomposed with the production of hydrofluoric acid, which takes up silica, and fluosilicic acid distills over.

In the first experiment, an iron retort was used, and in place of passing steam through the mixed ingredients, water was allowed to drop slowly on the hot materials through a safety tube. A small amount of weak acid was obtained, after which water distilled over. In the second experiment, the tube for introducing water was carried to the bottom of an iron retort. After a small amount of very weak acid had distilled over, the distillation ceased. An examination of the retort showed that the

iron tube passing through the materials in the retort, as also the retort, had fused. The iron had evidently melted below its usual fusing point, owing to the fluorspar acting as a flux.

Another experiment was made with an earthen retort of half a gallon capacity. A porcelain tube was passed through the tubulure of the retort to within an inch of the bottom. Fluor. spar and silica, broken into fragments of the size of large peas, were introduced into the retort, which was placed in a wind furnace, and a suitable condensing apparatus connected. When the retort had reached a full red heat, steam was introduced from a steam boiler, by means of suitable connection. For a short time the process promised well, then ceased.

An examina ion of the contents of the cold retort showed that the hot silica had been disintegrated by the steam sufficiently to pack the mass too tight for the vapor to penetrate it.

With this experience, I resorted to the process I had before employed for perchloric acid, which, although it claims no novelty, may interest some readers of the Journal from its details.

The first step, to obtain perchlorate of potash, is as follows: Heat in a porcelain crucible of 8 oz. capacity, over a gas furnace, eight ounces of chlorate of potash, until the salt is in complete fusion, taking care that but little or no oxygen is evolved. Then cover the crucible, and continue the same amount of heat till the fused salt thickens and crusts entirely over on top. A portion of the salt removed from the crucible should now impart but a light yellow color to pure undiluted muriatic acid. The crucible is now removed, and allowed to cool. When cold, the fused mass detaches itself completely from the crucible by turning it upside down.

Dissolve the mass in 2½ pints of boiling water. The perchlorate of potash crystallizes out on cooling, and should be washed with water to separate the mother water.

The loss of weight by heating the chlorate of potash was about two ounces in each pound. Amount of perchlorate of potash obtained from a pound of chlorate, about eight ounces. Four hours' heating was required for eight ounces of chlorate of potash, the gas flowing through a six foot burner, to about three-fourths of its capacity.

Perchlorate of potash is the most insoluble of all the salts of

perchloric acid, requiring 65 times its weight of water, at 60° F., for solution.

To obtain perchloric acid from perchlorate of potash, the salt is distilled (below the boiling heat of the ingredients) with twice its weight of sulphuric acid mixed with one-tenth part of water, as long as any distillate is obtained. The distillate, containing perchloric and sulphuric acids, together with some free chlorine, and a little hydrochloric acid, is treated with carbonate of lead rubbed into a paste with water, till baryta water no longer disturbs the clear solution. Should an excess of carbonate of lead have been used, the perchlorate of lead is to be carefully decomposed by sulphuric acid. The weak acid is now filtered from the sulphate and chloride of lead, and a few drops of hydrosulphuric acid added, to decompose the slightly soluble chloride of lead. After boiling, the acid is again filtered, and may now be concentrated in an open capsule below boiling until it attains a specific gravity of 1·6, or thereabouts, when it commences to give off white vapors. By distillation of this product an acid having the density of 1·693 is obtained.

One pound of perchlorate of potash yielded five ounces of acid of a density of 1·210.

The properties of perchloric acid have been so fully described by Prof. Roscoe, (vol. xxxiv. p. 64 of this Journal), that further notice is unnecessary.

The effect of this acid, sp. gr. 1·693, was tried on the following articles with morphia, codeia, narcotina, and atropia; no reaction. With

Meconin,	flesh color.
Quinia,	pale straw color.
Strychnia,	pale yellow.
Brucia,	rose color.
Delphia,	a dirty red color.
Aconitia,	a light ochry yellow.
Digitalin,	snuff brown.

Perchlorate of Morphia.

Dr. Ogden, in his analysis of chlorodyne, claims perchlorate of morphia as one of its ingredients. The following short no-

tice of this salt are the results of some experiments made to ascertain its character. It crystallizes in long acicular prisms. Requires 73 parts of water, and 44 of alcohol, at 60° F., for solution. In chloroform it is almost entirely insoluble.

NOTE OF CORRECTION ON PERMANGANATE OF POTASSA.

By Edward R. Squibb, M. D., of Brooklyn, N. Y.

In the experiments, upon which a paper on Permanganate of Potassa, in the September number of this Journal, was based, an important practical error occurred, which should have been earlier corrected.

The direction given in that paper to recrystallize the product first obtained was soon found to be not only unnecessary, but injudicious and wasteful, and it is the object of this note to correct this mistaken direction.

The "accumulated crystals in the funnel," if deposited from a clear solution, are, when carefully washed by percolation with distilled water, sufficiently pure for all ordinary purposes, though they do contain a very small proportion of free potassa. The writer now believes that Permanganate of Potassa cannot exist in hot solution under ordinary circumstances, without the presence of a definite, though small, proportion of free potassa. After the free potassa has all, or nearly all, been separated, a portion of the salt is decomposed into hydrated binoxide of manganese and free potassa, until the latter is again in sufficient amount to protect the remainder from decomposition. It thus happens that in attempting to recrystallize the well washed crystals, as directed in the published paper above referred to, great loss is unnecessarily occasioned. The formula and process may be very successfully carried out as published, if, to the six pints of boiling distilled water used to dissolve the washed crystals, half an ounce of solid caustic potassa be added, and the product will be exceedingly pure and nice. But for all ordinary uses the recrystallization may be entirely dispensed with, provided the process be well managed. A proportion of caustic potassa beyond that now indicated would, however, be very objectionable, as it would render the salt irritant and often hurtful.

It is questionable whether the excitant and stimulant action of the salt in its therapeutic uses be not due, in part at least, to the small proportion of free potassa always present or formed in the solution.

Brooklyn, December 16, 1864.

ON A TEST FOR THE RESIN OF CANNABIS INDICA.

By William Procter, Jr.

Having accepted the question, "Is there a reliable test for the active resin of Cannabis sativa of the East Indies, whereby the genuineness of 'Extract of Indian Hemp' may be satisfactorily and easily ascertained by the pharmaceutist?" the following paper is offered as a reply.

It need hardly be said that extract of Indian Hemp is a valuable medicine in the opinion of many practitioners, when prepared from hemp tops that have had their virtues developed by growth in a favorable climate and soil. In East Indian commerce there are three substances derived from the hemp plant, viz.: *gunjah*, consisting of the flowers and incipient fruit, with the smaller branches; *bang* made up of the leaves and capsules without the stalks; and *churrus*, the resinous matter secreted by the hemp plant under favorable circumstances. These have been long known in the East, but the form in which it has been chiefly employed by European and American practitioners, is the alcoholic extract of *gunjah*. The variableness in the medicinal power of this extract has been the cause of much disappointment to physicians; for whilst some samples prove effective in half-grain doses, *ten* or even *twenty* grains of other specimens have failed to produce its peculiar influence on the nervous system. The extract of commerce varies in consistence and color. Its green hue is sometimes much darker than at others, and its odor is equally variable in strength. Although professedly an alcoholic extract, much of it is but partially soluble in alcohol of 90 per cent. In a sample of extract, that had been imported several years ago from Mr. Squire, of London, in bulk, as much as 40 per cent. of the preparation was insoluble in stronger alcohol. The undissolved portion was brown, and readily soluble in water.

In another sample from the same House in ounce jars, the proportion of aqueous extractive was hardly noticeable. Another sample, the origin of which was not known, and which was quite old, had a solid consistence, almost black color, and produced powerful effects at the time it was tried therapeutically many years ago. No feature of this extract is more marked than its softness. After a pretty thorough examination of the subject, I believe this to be chiefly due to *fixed oil* of the hemp seeds, which the tops often contain sufficiently developed to yield oil, and which is, to a greater or less extent, extracted by the spirit, and being miscible with the resin, they remain in close union.

As regards the extractive matter soluble in water, its presence is easily accounted for, either by the use of alcohol weaker than ·835, or by following strong alcohol with weaker spirit to displace the former, when the process is carried too far. When officinal alcohol alone is used, it may occur by continuing the boiling process until the percentage of alcohol gets below the standard strength, as will occur with officinal alcohol during continued digestion. Where the proportion of matter insoluble in alcohol is as great as 40 per cent., either error or design must have produced it, as under no ordinary circumstances will hemp yield to alcohol such a product.

In the process of Mr. Robertson, of Calcutta, described by Pereira, in which the vapor of alcohol boiling in a still is conducted into the top of a cask containing the gunjah, with an ordinary condensing worm attached to the bottom of the cask, this may also readily occur; as the last portions of vapor from the still will be much more watery than the first, they will dissolve the extractive and carry it down into the recipient along with the resin, to be mingled with it in the subsequent concentration to the extractive consistence.

M. Gastinel, of Cairo, Egypt, has suggested that the resin should be washed with water to rid it of this extractive.

M. Laneau, of Brussels, after finding that hemp resin is much more soluble in a mixture of alcohol and ether or chloroform than in alcohol alone, recommends the hemp to be exhausted by percolation with such a mixture, which not only dissolves the resin better, but does not dissolve the inert matter.

Messrs. T. and H. Smith, of Edinburgh, who have studied hemp resin closely, have preferred to treat the gunjah first with water, and then with solution of carbonate of soda, to remove inert matter soluble in these menstrua, after which the hemp is dried and exhausted with alcohol. The tincture is then treated with milk of lime and filtered, and the dissolved lime separated by sulphuric acid. This treatment by lime is probably intended to remove fixed oil, and any other resinous matter than the active one, should any be present. The tincture is then decolorized by passing it through animal charcoal, evaporated to a syrupy consistence, and precipitated by water and dried. This process produces the pure hemp resin, but is far too tedious to pursue with the extract, which, if wholly soluble in alcohol of 90 per cent., is sufficiently freed from the inert matter of the gunjah. To obtain the answer to the query, it became necessary to secure an authentic specimen of hemp extract, which was obtained directly from gunjah of good quality.

One thousand grains of gunjah were reduced to powder, with the exception of the stalks, moistened with half an ounce of alcohol pressed in a funnel, the stalks thrown on the top, and the whole slowly percolated with alcohol of ·817 sp. gr. until eight fluidounces of the tincture had passed; the process was then stopped, and the tincture reduced to an extract by careful evaporation.

The product was soft, of a dark, dull green color, had the peculiar odor of hemp resin well marked, and weighed 110 grains, equal to 9 per cent.

It had the following properties:—

Soluble without appreciable residue, in strong *alcohol*, *ether* and *chloroform*. *Benzole* dissolved all but a small residue of blackish green matter, which is wholly soluble in alcohol; and on the evaporation of the benzolic solution, the resin retained its odor and other sensible properties.

Oil of turpentine dissolved it quite readily, and the solution, on standing, became coated with minute scaly crystals, the nature of which was not determined.

Olive oil dissolved it completely, forming a greenish solution, which has been suggested for pharmaceutical use by Laneau and by Githens.

Sulphuric acid acts slowly on the resin in the cold, more rapidly hot, without intumescence, and when diluted with water, a greyish precipitate falls.

Nitric acid, sp. gr. 1·38, when cold, slowly attacks the extract, but when heated, rapid reaction occurs, red fumes are evolved, and the resin is converted into an orange red resinoid substance, about as abundant as the resin treated. This, when washed with water and dried, has the appearance of minute fragments of gamboge, which it closely resembles in color.

This substance is readily soluble in alcohol, ether and chloroform, and does not crystallize from these solutions on evaporation; it is also soluble in solutions of potassa and ammonia and methylic alcohol, but is insoluble in benzole and acetic acid, and appears to possess an acid reaction with litmus.

Liquor potassæ acts but slightly on this extract, apparently removing little besides matter soluble in water, and, perhaps, fatty oil when present, and a part of the green coloring matter.

Of these reactions those best calculated to indicate true hemp resin extract, are:—

1st. Its odor when moderately heated.

2d. Its indifference to alkalies.

3d. Its solubility in alcohol, ether, chloroform, benzole and turpentine; and

4th. The reaction of nitric acid, which is the best marked test.

Before trying other resins it was deemed best to procure some American grown hemp, and make an extract from it with the same menstruum. Fortunately that this was easily accomplished, and the tops only of vigorous specimens of the cannabis were selected, dried and powdered. The color was deep grass green, the odor rank, but different from gunjah. Three hundred grains were reduced to powder, and treated with the same alcohol in like proportion as in the preceding experiment, and a soft extract, weighing thirty-seven grains, was obtained.

The color of this extract was a brighter green, and its odor quite different from the extract of gunjah; it rubbed down readily with liquor potassæ, making a dark colored liquid, not all in solution. When treated with hot nitric acid, rapid effervescence of nitric oxide followed, leaving a yellowish

liquid with a very small proportion of orange-colored resinoid matter, which appeared to be the same as that from Indian hemp.

It is very clear, from these results that the extract of common hemp may be easily detected by its solubility in caustic alkali, and the small portion of resinoid it yields by nitric acid.

1. The extract of Indian hemp before alluded to as being 40 per cent. of resin, was tried by these tests, and the resinous matter found to correspond with that made from gunjah.

2. Squire's extract in ounce jars afforded a large proportion of resin, which reacted with nitric acid like that obtained from gunjah.

3. A sample from my cabinet, fifteen years old, nearly dry, in dark greenish-black masses. This, when acted on by nitric acid, did not lose its greenish color, and altogether behaved differently from that made from gunjah.

4. Guaiac resin, treated with nitric acid, first became blue,—afterwards yellowish brown, but yielded no yellow resinoid.

5. Common resin yielded a yellowish resinous product by nitric acid, but entirely different from that obtained from hemp resin; in fact none of the resins tried have afforded a product similar to that from Indian hemp.

Whatever merit there may be in this test, it must be made more manifest by further experiments, with a series of extracts of known origin and therapeutic powers, so that it may be seen whether the results of testing are parallel with medicinal power: and the attention of members is invited to the subject, that they may, from samples tried by the physicians of their several neighborhoods, apply these tests, and ascertain their real value or accuracy.—From *Proc. Amer. Pharm. Assoc.*, 1864.

GLEANINGS FROM FOREIGN JOURNALS.

By Prof. F. F. Mayer.

On Chelidonic Acid.—C. Wilde (*Annalen der Chemie u. Pharm.*, Band cxxvii., page 164, August, 1863,) has examined the silver salt of this acid, and the action of heat and of bromine on the acid itself.

Chelidonate of silver has a composition expressed by the

formula $C_{14}H_3AgO_{12}+2HO$. It forms by a molecular change in the crystals of the basic salt, which is obtained by precipitating the salt of an alkali with nitrate of silver, and recrystallizing from a solution in dilute nitric acid. The tri-basic salts of this acid, which form on treating those containing two equivalents of the base with an alkali, possess a yellow color.

The acid crystallizes with 3 eq. of water for every two of acid. It effloresces in the air, and loses the whole of its water of crystallization over oil of vitriol or at 212° F. Heated to 292° F., it again loses water; at 428° F., it turns greyish and gradually still darker, and fuses with much frothing (from the escape of over 40 per cent. of carbonic acid) to a black mass, and a crystalline sublimate fusible at 136° F. The black residue contains an acid nearly corresponding to the formula $C_{30}H_{14}O_{28}$, which is soluble in water, but insoluble in alcohol.

Strong sulphuric acid destroys chelidonic acid on application of heat; the other mineral acids do not appear to act on it. Treated with excess of bromine in the presence of water at a moderate heat, decomposition, without evolution of gas, takes place. Hydrobromic acid is formed, a heavy oil remains in the retort, and another oil, heavier than water, passes over with the vapors of water. The residuary oil crystallizes in colorless radiating crystals from an ethereal solution; these have the composition of *pentabrom acetone*, $C_6HBr_5O_2$, from which it differs only by its fusing point being much higher, and its greater resistance to the action of heat. The residuary liquid likewise contains *oxalic acid*. The heavy liquid which passes over appears to be *bromoform*.

An apparatus for the fractional distillation of bituminous coals, shale and mineral oils, etc., has been contrived by Regnault for the use of the French Customs and manufacturers, and is described in *Annales de Chimie et de Physique*, *Tome* 68, *p.* 409, and Fresenius' *Zeitschrift fur Analytische Chemie*, 1864, *p.* 357. Here it is used by the rectifiers of petroleum, and is for sale by Luhme & Co. in New York.

The apparatus consists of a small upright cylindrical copper still, with a tubulus on top for the introduction of the oil, and for the insertion of a cork with a thermometer for determining the boiling point. The beak is a narrow tube soldered to the

side below the tubulus, and fits into an adapter-tube attached to an upright cylindrical condenser made of brass, which ends both above and below into a narrow tube, the latter to carry off the condensed products, the other as a safety-tube. The condenser is enclosed in a brass or tin cooler with supply and overflow pipe for water, to which it is fastened by the descending and the adapter tube, which pass through the cooler. The whole is supported by a tripod bearing the cooler, attached to which is also a holder for the lamp. The tripod also carries below a horizontal shelf, on which a tube-stand moves in a slide, there being five tubes marked each for 100 cubic centimetres; these are intended to receive the various quantities of oil, which distil over at or between certain boiling points. The retort is not to be charged to more than one-third its capacity; the bulb of the thermometer must not be allowed to dip into the oil, but its scale below the mark of 80° C. must not be visible above the cork.

This contrivance may be made to answer some purposes in a pharmaceutical or technical laboratory besides the one for which it was originally intended.

Sublimation of Alkaloids.—Dr. Helwig, of Mayence, has published (in Fresenius' *Zeitschrift*, 1864, p. 43) researches on microscopic tests applicable for diagnosis, and among these describes the *sublimation* of nearly all medicinal alkaloids, which he states, when properly treated, furnished perfect objects for micro-chemical examination. The alkaloids in the form of fine powder, are heated very carefully on a piece of platinum foil, hollowed out somewhat, and covered with a plain glass plate.

Most of the sublimates are stated to be crystalline; those of morphia and strychnia are obtained with especial facility, and allow the application of all the usual tests. They are readily distinguished by a dilute solution of chromic acid, which forms crystals with strychnia, but not with morphia. Brucia does not yield so readily a crystalline sublimate, nor is the reaction with chromic acid as distinct. Veratria, solania and aconitia also give crystalline sublimates; the product in the latter case is perfectly soluble in ammonia, from which solution it again crystallizes on evaporation. Atropia is very easily destroyed when too high a degree of heat is employed; when carefully

treated a sublimate is obtained, consisting of clear, colorless drops, which form crystals with the acids. Digitalin likewise yields such a product, the nature of which could not be ascertained as satisfactorily, though it appeared to form crystals with some of the acids.

Comparative value of Narcotic Extracts and Alkaloids.—We extract some portions from a paper read early in 1863, by Alois Jandous, before the General Society of Austrian Apothecaries. The author refers to the varying statements made by different writers, and often by one and the same, in regard to the quantities of alkaloids contained in the extracts of which they are assumed to be the active ingredients: Thus, while Rabourdin quotes an extract belladonnæ with ·53, and another with ·05 per cent. of atropia, Mein gives the yield of pure atropia from the leaves as ·02, and Procter that of the root as ·33.*

This statement of Rabourdin probably refers to crystallizable atropia, since it must be assumed that extract of good quality was employed, which, as regards activity, ought to surpass the leaves or root. The only cause necessary to adduce for such discrepance is the facility with which this and other alkaloids of the Solanaceæ, and other organic compounds, are decomposed in contact with moisture, air and heat; for atropia, when left standing but a short time under, or dissolved in water, ceases to be crystallizable. From 0·1 gramme of crystallized atropia which had been precipitated by tannin, after decomposition of the precipitate with oxyd of lead and extraction with alcohol, but ·056 grm. were recovered, and that in the amorphous condition. An extract of belladonna, which had been prepared a year before from the coagulated juice, yielding 2½ per cent.,

*[Brandes gives 1·51 per cent. of malate of atropia in the leaves. As by the Prussian method of preparing the extract of belladonna from fresh leaves, viz: treatment of the inspissated juice with strong alcohol, the yield is from 3½ to 4 per cent. of extract, this latter, adopting the lowest statement, that of Mein, should contain at least 6 per cent. of atropia. Mayer, of Heilbronn, obtained 1¼ per cent. of pure alkaloid from extract, or ¼ per cent. from the dried root. Geiger estimates 200 grains of extract equal to one grain; Schroff the same quantity, equal to 7 grains. The best American alcoholic extract (U. S. P., 1860) yielded from 2 to 3 per cent. of impure atropia, of which not one-third was crystallizable.]

was treated with ether, alcohol and caustic lime and gave 3·8 per cent. of a brown, amorphous mass, which again yielded a precipitate of tannate corresponding to 1·9 per cent. of atropia. The same extract, by comparing it approximately with a solution of the pure sulphate, previously tested with one of biniodide of potassium, showed that it ought to have contained 5 per cent. of atropia. It appears, however, more probable that the quantity of the alkaloid should be assumed as 2, or rather 3, per cent., the precipitatior by tannin being not perfect. Of an extract of this strength the maximum dose of 2 grains then corresponds to ·16 grain of atropia.

Hyoscyamia, which is described as a crystalline substance, the author was unable to obtain in any other form than that of volatile oily fluid, having a strong odor of tobacco. From a soft extract, prepared from the fresh flowering herb, which had yielded 2·6 per cent., ether and potassa, extracted only 0·46 per cent. of this oily base. An alcoholic extract, made from the same herb, of which it had produced only ¼ per cent., after treatment with subacetate of lead, sulphuretted hydrogen, caustic lime and ether, yielded a still more impure product. The greater percentage of hyoscyamia in the latter extract, which should have been 3 or 4 times that of the former, must have been destroyed by the process of eliminating it.

Extract conii, which was a yield of 3·9 per cent. from the flowering herb, gave 3 per cent. of pure conia. It should be noticed that the alcohol recovered from the evaporation of alcoholic extracts contains perceptible traces of volatile alkaloid.

The Raphides or Crystals in certain Vegetable Drugs.—Prof. Berg, as well as Flückiger, some time ago declared the crystals found in abundance in South American soap bark to be those of gypsum. Blekrode and Martius afterwards stated that they were carbonate of lime (arragonite); but Kindt lately showed that they contained no sulphur, but were soluble in hydrochloric acid, and no doubt consisted simply of oxalate of lime, a fact which Flückiger now confirms, (*Schweiz. Wochenschr. zeitung. N. D. Apoth. Verrin.*, March 31, 1863.) On examining the crystals found in the bark of guaiac, which Guibourt had declared to be benzoic acid and Berg as another occurrence of gypsum, Flückiger discovered them to be the ordinary oxalate

of lime, with probably a trace of the sulphate of an alkali. The same appears to have been observed by Scheele. Guaiac wood and its bark show besides a remarkable difference in the respective quantities of ashes which they yield: the splint or colorless part left ·916 per cent. of ashes; the central, dark-colored and resinous wood only ·6 per cent. The bark of quassia, which is likewise rich in oxalate of lime, leaves 17·84 per cent., the wood only 3·68 per cent. of ashes. The crystals contained in tamarinds Flückiger declares to be those of *tartrate of lime*. The latter salt is likewise present to a considerable extent in the quillaya bark; the ashes of the latter contain traces of lithium, and probably rubidium.

Oxalate of lime, either in the form of acicular, prismatic, or rhomboidal crystals, is contained also in *Cort. Swieteniæ Senegal*, *Cort. Strychnos*, *N. Vom.*, *Pareiræ*, *Colombæ*, *Hippocastani*, *Pruni Padi*, *Cedrelæ*, *Scillæ*, *Colchici*, *Veratri* [*albi* (?)], *Chinæ*, *Sarsaparillæ*, *Polygonati*, *Paridis*, *Iridis Flor.*, *Belladonnæ Geoffroyæ*, *Simarubæ*, *Lopez*, *Cascarillæ*, *Cinchonæ*; also, in *Rad. Rhei* and other *Polygonaceæ*, *Saponariæ*, *Convolvuli Orizab.*, *Cort. Granat. Rad. etfructus*, *Rad. Ipecacuanhæ*, *Rubiæ*, *Ipomoeæ Mechoacanæ*, but not in the officinal tubers from *Exogonium Purga*. Benth.

Test for Tartar Emetic.—As such C. Claus (*Pharm. Zeitschrift f. Russland, No.* 12. *Schweizer Wochenschrift f. Pharm.* 1863, p. 135) recommends the solution of perchloride of iron, which produces a peculiar reaction with not too strongly acid solutions of tartar emetic, as a test, that serves to distinguish it quite readily from all other officinal preparations of antimony. The solution of iron added to a concentrated solution of the tartar emetic merely gives it a yellow tinge, but when the solution is largely diluted with water there forms at once a yellow precipitate of the color of chromate of lead. In a very dilute solution a single drop of the iron liquor produces at once this precipitate, which, what must be carefully observed, is readily soluble in an excess of the reagent. If less than sufficient of the latter is added to redissolve the precipitate, it assumes a gelatinous consistence. It is principally oxychloride of antimony colored by iron, and contains a little tartrate of antimony and potassa, which cannot be removed by washing.

RESEARCHES ON THE RESPIRATION OF FLOWERS.

By M. Aug. Cahours.

While the green portions of plants under the influence of light effect the decomposition of carbonic acid, of which they assimilate the carbon, rejecting the oxygen into the atmosphere, the colored parts, on the contrary, consume the oxygen to produce carbonic acid. Thus, by one of nature's most admirable harmonies, the atmosphere does not, after ages, become sensibly modified.

But if experiment has long since proved that flowers left in atmospheric air develop carbonic acid at the expense of the oxygen it contains, it is, nevertheless, interesting to determine the modifications presented by this phenomenon under varying circumstances.

Now, do all flowers of equal weight, or of equal surface consume, under identical circumstances, the same quantity of oxygen, and produce the same proportion of carbonic acid? Do scented flowers behave in the same way as those which are scentless? Does the same flower act more energetically on an atmosphere determined under the influence of a more or less vivid light than in perfect darkness? Is the consumption of oxygen proportionate to the temperature of the medium in which the flower respires? Does a plant consume the same quantity of oxygen at each period of its development? Finally, what do the various parts of the plant—the calyx, corolla, pistil, stamens—respectively play?

Such are the questions I propose to resolve.

If we experiment on various flowers of equal weight, arrived at the same state of development, it is easy to ascertain, by operating under perfectly identical conditions, that the respective consumption of oxygen in a given time is far from being the same. As to the more or less powerful odor exhaled by the plant, it seems to play but a trifling part in the production of this phenomenon; in fact, a scentless, or nearly scentless, flower consumes, in a given time, more oxygen than a strongly scented one. Results obtained at the beginning of these researches led me at first to suppose that scented flowers

absorbed atmospheric oxygen more rapidly; but later and multiplied experiments on various flowers have shown me that this view could not be established as a general conclusion.

On the other hand, I am convinced that, other things being equal, though the proportion of carbonic acid formed is generally rather greater when the flower is exposed to the light than when it is in perfect darkness, the difference is far from being so great as is supposed. This difference becomes much more manifest when the normal air is replaced by pure oxygen.

When the phenomenon takes place in ordinary air, it is not unusual to find that the results are the same, whether obtained in darkness or in a bright light. This result is very different to those obtained with most organic substances, which, enclosed in equal weights in tubes containing equal volumes of atmospheric air, consume much more oxygen in light than in darkness. The differences observable under these circumstances may probably be accounted for, in the one case, by the bodies undergoing change being possessed of more or less energetic vitality, and in the other being entirely inert.

In operating on the same plant, either in complete darkness or in the light, it is found that as the temperature is raised, the proportion of carbonic acid produced in a given time is very appreciably augmented. This result is observable in the most various flowers. When the outer temperature varies from + 15 to + 25°, the transformation of oxygen into carbonic acid is rapid; but with temperatures between + 5 and + 10°, it is, on the contrary, slow.

The plant does not consume the same quantity of oxygen at different periods of its development, nor produce the same proportion of carbonic acid. Such is the result of a large number of comparative experiments. The differences are, nevertheless, not very considerable. By gathering from the same plant exactly equal weights of buds and full-blown flowers, and placing them respectively in equal volumes of normal air under identical conditions of light and temperature, the consumption of oxygen is almost always slightly greater with the buds than with the full-blown flowers,—a result which is not surprising when we consider that the vital force is greater in the first than in the second instance; still, the difference is never very striking.

Now, all plants being composed of several distinct parts, it may be asked, "What part is taken by each portion in the production of the phenomenon?" To ascertain this, it is necessary to anatomize the flower—to isolate its various parts, to study the part each plays—by putting them respectively in contact with known volumes of normal air—taking their respective weights into consideration—and comparing the results given by the various parts, with the general results derived from the entire plant, the experiment being, moreover, effected under perfectly identical circumstances.

By operating thus on flowers with sufficiently developed pistil and stamens, the weight of which is not a fraction too small for that of the entire flower and the corolla, such as the oriental poppy, the field coquelicot, the coquelicot with large bracts, the lily, the water lily, &c., I found that on comparing the proportion of carbonic acid furnished by the corolla with that given, under the same conditions, by the pistil and stamens, there was a great difference in favor of the latter—a result which might, indeed, have been expected.

Finally, independently of the carbonic acid formed by the combustion of the elements of the flower at the expense of atmospheric oxygen, this gas itself disengages a certain proportion, as may be ascertained by leaving the flowers in an apparatus containing inert gases, such as hydrogen or nitrogen.

In conclusion, I summarize thus:—

1. That all flowers left in a limited atmosphere of normal air consume oxygen, and produce carbonic acid in proportions varying as the flower is scentless or not.

2. That the circumstances under which the phenomenon takes place being identical, the proportion of carbonic acid increases as the temperature is raised.

3. That generally with flowers from the same plant and of equal weight, the quantity of carbonic acid produced is rather greater when the apparatus in which the experiment is performed is exposed to the light, than when it is in darkness; that the proportion is, nevertheless, sometimes the same under either condition.

4. That when the normal air is replaced by pure oxygen, the differences become much more marked.

5. That buds produce rather more carbonic acid than fully-developed flowers, which is explicable by the greater vitality of the buds.

6. That flowers left in inert gas disengage small quantities of carbonic acid.

7. Finally, the pistil and stamens, which possess the greatest vitality of any part of the flower, consume the greatest quantity of oxygen, and produce the largest proportion of carbonic acid.—*London Chemical News*, No. 251, from *Comptes Rendus*, lviii. 1206, 64.

ON PYROXYLIN.

By MM. Pelouze and Maurey.

The attempts made during the last twenty years to substitute gun-cotton for ordinary powder for fire-arms and mines have resulted in most opposite conclusions. In France, after numerous experiments, it has been discarded on account of its detrimental effect on the metal of fire-arms and accidents from spontaneous combustion and explosion, first brought into notice by a memoir presented by us to the Institute in 1849.

In Austria, General Lenk has continued to occupy himself with the manufacture and use of this explosive material. He prepares it by a process which has been followed on a large scale at Hirtenberg, and which remained for some years a profound secret. But during the last year, papers on this subject have been published by German chemists and by General Lenk himself.

It would appear from these papers that the Hirtenberg pyroxylin does not decompose spontaneously, like that made in France at the Bouchet powder factory, and, moreover, differs from the latter in its composition, and in the circumstance that its explosive power may be regulated by particular arrangements. We will now examine the value of these assertions, giving the results of some experiments and analysis we have made with the co-operation of MM. Faucher and Chapoteaut.

Processes followed at Hirtenberg and at Bouchet.—The pyroxylin made at Hirtenberg by General Lenk's process, is like

the Bouchet pyroxylin, the product of the immersion of cotton in a mixture of monohydrated nitric acid and sulphuric acid at 66°. The two methods, however, differ in several respects.

Thus, the proportions of the two acids are not exactly the same, Lenk's mixture being composed of one part of nitric acid to three of sulphuric acid; that of Bouchet, under the name of unequal volumes, is prepared with one part of the first of these acids and two of the second, equivalent in weight to 1 per 2·46. The above-mentioned memoir gives as being most successful a mixture of three volumes of nitric acid and seven of sulphuric acid (by weight 1 to 2·86), proportions very nearly those given by General Lenk.

At Hirtenberg the cotton is steeped in portions of 100 grammes in 30 kilogrammes of the mixture. It is withdrawn from the bath after being shaken in it for an instant, and each time the quantity of mixture absorbed by the cotton is replaced by a fresh amount. These operations are continued indefinitely, the weight of the mixture being always 300 times that of the cotton.

When the desired quantity of cotton has been steeped, it is put into a receiver and allowed to remain forty-eight hours impregnated by the acids. It is then placed in a strainer, where most of the uncombined acids are expelled in a few minutes.

It is freed from the remainder in a stream of water in which it is washed, and where it remains immersed for six weeks, when it is strained a second time, boiled for two or three minutes in a solution of carbonate of potash of 2° Baumé. After a third and last straining the cotton is dried in the air if the weather is favorable; if not, in a stove of which the temperature is not allowed to exceed 20° C.

General Lenk has latterly made use of a solution of soluble glass of 12° Baumé. The cotton prepared as above is soaked in it, dried, and exposed to the air for a sufficient time to allow the carbonic acid of the atmosphere to combine with the soda of the glass, which determines the precipitation of an insoluble silicate, which, according to General Lenk, "encloses the fibres of the cotton, and prevents the development of gases."

At Bouchet the cotton is steeped in vessels containing only 2 litres of mixture for 200 grammes of cotton, and the steeping is considered complete at the end of an hour.

About 70 per cent. of non-combined acids are pressed out, the cotton being then watched for one or two hours in the river, freed from most of the water by strong pressure, and left for twenty-four hours in an alkaline ley to neutralise the last traces of acids. Withdrawn from this, it is a second time washed in the river, then pressed, and finally dried on a light canvas, through which a ventilator forces cold air.

Soluble glass has not been tried at Bouchet, but we are about to show that it is not so beneficial as it is supposed to be by General Lenk.

Quantity of Pyroxylin produced by a given quantity of Cellulose.—A German report signed by MM. Redtenbacher, Schrotter, and Schneider gives to Lenk's pyroxylin the formula—

$$C_{12}H_7O_7.3NO_5 \text{ or } C_{12}H_73(NO_4)O_{10},$$

equivalent to the following composition :—

Carbon	24·24
Hydrogen	2·36
Oxygen	59·26
Nitrogen	14·14
	100·00

The reaction may be explained in two ways : —

1. By admitting that by contact with the mixture of nitric and sulphuric acids the cotton loses the water, which is replaced by the first of these acids—

$$C_{12}H_{10}O_{10}+3NO_5=C_{12}H_7O_7.3NO_5+3HO.$$

2. By supposing that the hydrogen of the cellulose is replaced by an equal number of equivalents of hyponitric acid—

$$C_{12}H_{10}O_{10}+3NO_5=C_{12}H_73(NO_4)O_{10}+3HO.$$

According to this 100 parts of cotton ought to produce 183 of pyroxylin; but though in more than 100 experiments we have varied the proportions of the bodies producing this explo-

sive matter, 178 is the greatest yield we have been able to obtain.

The German report is silent on the subject of the yield, which, in our opinion, constitutes the most solid basis for determining the composition of pyroxylin. We do not say that the exact determination of the yield of cotton in pyroxylin renders useless the elementary analysis of the latter, but it is necessary that the analysis should agree with the figures representing this yield.

Our experiments on the yields have been made with cotton of good quality, previously washed in a boiling solution of carbonate of potash or soap, and then freed as much as possible from foreign bodies, particularly from cotton seeds. Before being used it was carefully dried in a Gay-Lussac stove, between 100° and 115°

The sulphuric acid marked 66° on the Baumé areometer. The nitric acid had a density of 1·500 at 9°; it was yellow and slightly nitrous.

The relative proportions of the sulphuric and nitric acids were varied so as to present—1. The composition of Lenk's mixture; 2. That of the unequal volumes of Bouchet; 3. Various intermediary proportions between 2 and 3 of sulphuric acid for 1 of nitric acid.

The relative proportions of acid mixture and the weight of cotton were also varied, including those formerly used at Bouchet, and those indicated by General Lenk, until the weight of the acids was 500 times that of the cotton.

The duration of the immersion of the cotton in the acids varied from 1 to 66 hours.

In all these experiments the yields differed very little, never exceeding 178 per cent. of cotton.

The yield in manufactories whether at Hirtenberg or Bouchet is far from being so large as that obtained with small quantities in the laboratory. In fact, General Lenk says that it requires 64·500 kils. of undried cotton to produce 100 kilogrammes of pyroxylin, which corresponds to a yield of 155. Supposing the cotton to contain 6 to 7 per cent of moisture, the yield of dry cotton at Hirtenberg would have been from 165 to 167 per cent.

The yield at Bouchet, after the working had become regular, was 165·25 per cent.

Though unable to draw from these numbers any conclusion as to the theory of the formation of pyroxylon, we cannot pass over in silence a circumstance as important as the yield, so as to speak identical with it, obtained on a large scale in the two factories.

(To be continued)

PRELIMINARY NOTICE OF A NEW EARTH.

By M. Ch. Bischof.

In treating a calcareous mineral by the ordinary re-agents, M. Ch. Bischof has discovered an earthy substance which, by its chemical properties, appears to differ from all the other known earths. The following are the different characters assigned to it by the author:

The new earth is precipitated by sulphide of ammonium; it is more completely precipitated by potash than by ammonia. The precipitate is bluish white, gelatinous, and dissolves sensibly in water. An addition of tartaric acid does not prevent it forming. It is almost completely soluble in carbonate of ammonia. This solution is precipitated by oxalic acid. When this precipitate is intimately mixed with carbon, and the mixture heated in a current of dry chlorine, the chloride of the new base is seen to volatilise; the sublimate obtained is more volatile than chloride of iron. But what characterises more particularly this substance is the manner its chloride comports itself at a high temperature. Heated strongly, the salt splits into a portion which sublimes in form of a white deposit, and a portion which remains and which presents the characters of a base.

The blowpipe and spectroscope failed to give any decisive reactions. The volatility of the chloride, and the solubility of the oxide in water have prevented M. Ch. Bischof obtaining a large quantity of the earth in question, but he promises a further communication.—*Chem. News, October* 22, 1864, *from Cosmos, October*, 1864.

REPORT ON THE PURITY OF SULPHATE OF QUININE OF COMMERCE.

BY MR. W. WALTER STODDART.

(*Read at the Bath Meeting of the British Pharmaceutical Conference, September*, 1864.)

Probably quinine is one of the most important therapeutic remedies for the ills of the human body that has ever been introduced to the notice of the medical man; so extensively is it used, and with such certainty may its effects be calculated, that no other substance can be advantageously substituted. Yet this very circumstance unfortunately gives the temptation for frauds and adulterations so commonly said to be practised by unprincipled dealers.

The smallness of the dose with which quinine gives such remarkable results, renders any sophistication all the more dangerous, and disappointing to the physician; indeed, the very turning-point of an illness may be frequently dependent on the purity of a sample of quinine.

It is not by any means to be supposed that any suspicion is attached to the high respectability and probity of the well-known manufacturers of quinine. Existing adulterations, properly so called, such as the deliberate addition of salicine, sugar, boracic acid, quinidine, cinchonine, etc., are only made by second or third-rate dealers, or when it has passed through the hands of a third or fourth party. Such samples may still be found in shops situated in secluded parts of the country or lowest streets of a city, and traceable to the same origin.

On the other hand, probably from difference in the mode of preparation or separation of the cinchona alkaloids, quinine differs much from the presence of its isomeride quinidine. The latter is often, if not always associated with quinine in the natural state, and has many of its reactions exactly similar, besides being nearly as soluble in the usual menstrua.

It therefore becomes to a certain extent a natural mixture, and in proportion to the completeness of the extracting process, so will be the purity of the product. Opinions, it is true, vary greatly as to whether quinine and quinidine differ in their medicinal power, and therefore some may say that the presence of

the latter (quinidine) is of no consequence; this, however, is not the question at issue, and the points of this report are strictly confined to the commercial purity of quinine and its freedom from the cheaper salts.

In carrying out this object the desired results are threefold:—

First, *Qualitative*, or to find an easy and reliable test for the presence of the three most common cinchona alkaloids, quinine, quinidine, and cinchonine.

Secondly, *Quantitative*, to find the most practical and reliable mode of separating and estimating these alkaloids; and

Thirdly, an application of the above to the examination of the sulphate of quinine as made by the principal manufacturers.

Although the cinchona barks contain many alkaloids, only four occur in sufficient frequency and quantity to merit notice in a commercial investigation—quinine, quinidine, cinchonine, and cinchonidine. In actual practice the two last may be estimated together.

The most prominent impurity in quinine is quinidine; in none of the after-mentioned samples was cinchonine discovered in any quantity except one. The slight solubility of the cinchonine salts as compared with those of quinine and quinidine, and the boldness of its crystallization would, to the practiced eye, soon lead to its detection; experiments will easily show the truth of this, and that quinidine and not cinchonine must be generally sought as the chief impurity in commercial sulphate of quinine.

Notwithstanding tests for the purity of quinine are so numerous and in some instances so trustworthy, still few apply to the *separation of quinidine* from quinine; nearly all are proposed for the indication of quinine only, or its detection when mixed with other substances.

The polariscope tests of Bouchardat and Pasteur, and the fluorescent test of Professor Stokes, require too much study and practice to come into general use for qualitative analysis among manufacturers and retailers.

The same remarks apply to the exquisitely beautiful experiments of Dr. W. B. Herapath. It is quite true that to the expert the iodide test will detect the presence of a very minute portion

of quinine, quinidine, or cinchonidine, yet it requires considerable experience with an expensive polarizing microscope, with great consumption of time, to give good results, when only a minute quantity is operated on.

The chlorine and ammonia test of Brande, and the chlorine test of Pelletier, will not distinguish always between quinine and quinidine.

The presence of so much water and ammonia is detrimental to the British Pharmacopœia test, which is anything but a good modification of Liebig's original one.

From these remarks it will be apparent that a good qualitative test for detecting the several cinchona alkaloids in an unknown mixture is a desideratum. From a considerable series of experiments it appears that these conditions may be amply fulfilled by either of the two following methods:

The first is a modification of that proposed by Liebig.

Into a glass tube or bottle put ten grains of the suspected salt, dissolve in ten minims of dilute sulphuric acid and 60 minims of distilled water; to this add 150 minims of *pure* sulphuric ether, three minims of alcohol, and 40 minims of a solution of hydrate of soda (1 part to 12 parts). Agitate well and lay aside for 12 hours, when, if the slightest trace of quinidine, cinchonine, or cinchonidine be present, they will be seen at the line of separation between the ether and solution of sulphate of soda.

If only a small percentage of quinidine be present, it will appear as an oily substratum, appearing under the lens as dust from the minuteness of its particles. Cinchonine will appear more decidedly crystalline. With a little practice, the eye will easily distinguish which of the alkaloids is deposited.

This will detect a much less quantity of quinidine than the Pharmacopœia test. In the latter the ether dissolves a greater portion of the quinidine, while the dilute ammoniacal solution of sulphate of ammonia is an actual solvent, unless great care be taken to add no more ammonia than will exactly precipitate the alkaloids, which is often difficult and tedious.

The second method proposed is the one most generally used by the author, and which is perhaps the easiest and most

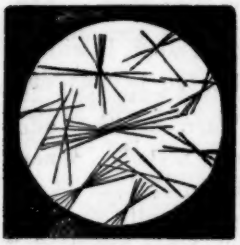
trustworthy of any hitherto submitted. The reagent is sulphocyanide of potassium.

Into an ounce of distilled water drop ten drops of dilute sulphuric acid (British Pharmacopœia $\frac{3}{35}$). To this add 14 grains (or as much as will saturate the acid) of the suspected salt. Filter through paper, and to a little of the filtered solution add a few drops of the solution of sulphocyanide of potassium (180 grains in $1\frac{1}{2}$ ounces of water). An immediate precipitate of the several alkaloids takes place, each of which, as seen by the sketches, is distinct and characteristic.

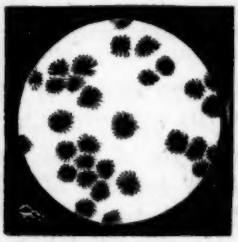
If quinine, quinidine, and cinchonine be present they will all be seen on the slide distinct from each other, becoming more so every minute.

A very good plan is to place a very small drop on a glass slip and to put another of the sulphocyanide by its side. Over both place a piece of thin glass, which will cause the drops to touch. Examine the line of junction under a quarter-inch lens, when the crystals are seen and may be readily recognized. By this method $\frac{1}{10000}$ of a grain of quinidine or cinchonine may easily be detected.

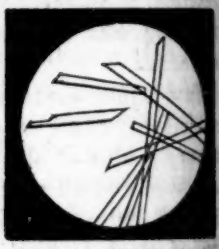
It is very interesting to see the particles all arranging themselves into the respective groups; the long slender needles of the quinine salt, the round crystalline masses of the quinidine,



Sulphocyanide of quinine. (450 diam.)



Sulphocyanide of quinidine. (450 diam.)



Sulphyocyanide of cinchonine (450 diam.)

and the large well-formed prisms of the cinchonine salts. So remarkably constant is this reaction, that an observer who has once been accustomed to the general appearance can at once say with ease, this is quinine, this quinidine, and that cinchonine.

Sulphocyanide of potassium is not usually kept by druggists, but may readily be made thus :—

Cyanide of potassium (fused),
Sublimed sulphur, of each 120 grains.
Distilled water, an ounce and a half.

Boil in a glass flask for fifteen minutes, filter, and make up the quantity to 1½ ounces with sufficient distilled water.

This notice of the qualitative analysis ought not to be passed without mentioning a very good application of Prof. Stokes' fluorescent test for the discovery of quinine and other substances possessing the property of epipolism.

A small Geissler's vacuum tube is surrounded by a longer glass tube which is capable of being closed by a cork, an arrangement that permits the tube to be filled and emptied as an ordinary phial bottle. When any bark is suspected to contain quinine, etc., an acid or alcoholic infusion is put into the outer tube, and a spark from the Ruhmkorff's coil passed through. Instantly the fluorescent salt, whatever it may be, will show its presence in the most gorgeous manner.

By this method twenty-seven samples of barks were qualitatively tested in a couple of hours that were supposed to contain a new alkaloid, which occurs in on Australian tree possessing very peculiar fluorescent properties.

The process most applicable for the quantitative analysis of sulphate of quinine is that by means of the iodide of potassium reaction, recommended by Dr. De Vry some time since. The following was the arrangement employed in the present instance :—

Into a tube containing 120 minims of distilled water and 16 minims of dilute sulphuric acid (British Pharmacopœia), add twenty grains of the sulphate of quinine to be tested. When dissolved add 80 minims of solution of hydrate of soda (1 to 12) and 300 minims of *pure* sulphuric ether mixed with six minims of alcohol.

Agitate well, and lay aside for twelve hours ; decant the ethereal solution and evaporate for the *quinine*. To the remaining aqueous solution add just sufficient acetic acid to neutralize the alkali, and precipitate with solution of iodide of potassium (1 to 4), filter, dry, and weigh the hydriodate of

quinidine. One hundred grains of this salt contain 71·68 of pure *quinidine*. To the filtered solution again add hydrate of soda till decidedly alkaline, when the cinchonine and cinchonidine will be precipitated if present.

It was according to the above-mentioned process that the following samples of quinine were analyzed. The first was taken from a four-ounce bottle from Messrs. Howard's and Sons, Stratford.

On submitting it to the soda and ether test there was no appearance of cinchonine, but beneath the ether was an oily substratum, which by the usual tests was proved to be quinidine.

The quantitative analysis showed this to amount to 2·8 per cent. After the separation of the quinidine the soda gave no precipitate, proving the absence of cinchonine and cinchonidine Consequently this was an extremely pure sample of sulphate of quinine.

The next sample tested was quinine from the laboratory of De Lisle and Co., Paris, better known as "Pelletier's quinine." This yielded 4·1 per cent. of quinidine, and the soda gave a trace of cinchonine.

The third sample was from the chemical works of Mr. Jacob Hulle, Lombard Road, Battersea. This contained 5·6 per cent. of quinidine and ·8 per cent. of cinchonine and cinchonidine.

The unbleached variety of the same maker was, as may be expected, much less pure than any of the above.

The sample examined contained 16·3 per cent. of quinidine and 4·2 per cent. of cinchonine and cinchonidine. All these were taken out of bottles unopened and sealed by the manufacturer.

With neither was there any precipitate with nitrate of silver and nitric acid, proving the absence of muriate of cinchonine; neither did strong sulphuric acid produce any tinge except the usual pale yellow tint.

A quinine has lately been introduced by Messrs. Herring and Co., Aldersgate Street, under the name of "semicrystallized quinine," but as it does not profess to be pure sulphate of quinine, but a compound of *all* the alkaloids of the yellow cinchona barks, it ought by no means to be used by the dispenser

as a substitute for quinine without the sanction of the prescriber. The same remark applies to the unbleached variety of Mr. J. Hulle.

A sample from Germany was also examined and found to be exceedingly impure, but as it was not an original package, and without any name, it was thought inexpedient to bring it before the notice of the members of the Pharmaceutical Conference. It is very gratifying to be able to affirm that sulphate of quinine, if purchased in bottles or sealed packets, as sent out by the makers, or obtained through our well-known wholesale houses, is commercially pure and quite fit for medicinal use.

It must be the chemist's own fault if he is imposed upon, and not supplied with an article of sufficient purity.—*London Pharm. Journal*, Nov. 1, 1864.

ON THE EXTRACTION AND PRESERVATION OF AROMATA.

By Charles R. C. Tichborne, F.C.S.

chemist to the apothecaries' hall of ireland, etc.

(Read at the Bath Meeting of the British Pharmaceutical Conference, Sept., 1864.)

Some time ago I noticed in my garden a vegetable curiosity of some interest. As I was desirous of preserving this *lusus naturæ*, I submerged it in some weak glycerine, considering that that fluid would be less likely to shrivel the tender stems, and also remembering that it had been found most efficient in the preserving of animal tissues.*

The glycerine answered its purposes admirably, preserving the delicate parts in all their *contour*, and at the same time preventing decomposition.

I immediately saw that this property of glycerine might be made available for certain pharmaceutical processes where it is desired to preserve or to extract the aromata of vegetable products, *i. e.* it is applicable to the preserving of elder, orange, or rose flowers; and also, as will be shortly explained, it may be substituted for the oils and fats used in the process termed *enfleurage*.

Flowers for making the officinal *Aqua Sambuci* may be pre-

* Experimeats of M. De Marquay, "Journal de Chimis Médicale."

served for an indefinite period, the following being the mode of operating:—The elder-flowers should be gathered when the corolla is fully expanded, but not too far gone; they should then be plucked from the stem and packed firmly in wide-mouth bottles or jars without crushing them, and finally be well covered with glycerine and corked. It is not necessary that the glycerine should be pure for this purpose, but it should be devoid of odor and have a high gravity (about 1·240 at 60° F.).* The common glycerine made from soap or plaster has generally a slight odor, which must be got rid of before it is used for this purpose. When they are wanted for the distillation of the water, the flowers with the glycerine are put into a still, or what is preferable, the glycerine is expressed and is then found to be saturated with the otto. Water is then added, the quantity being regulated by the original weight of the preserved flowers, or the amount it is determined to distil. I have preserved flowers for two years, and on distilling them this summer I have procured a water, the perfume of which equalled that made from flowers of this season.

As the essential oil seems soluble in all reasonable proportions, this is a very convenient method of making a concentrated water, either by treating the glycerine after expression with a fresh portion of flowers or by regulating the amount of water added on distillation. This process of preserving flowers will be found to far exceed the old plan of preserving them between layers of salt, particularly as it is almost next to impossible to distil the flowers so preserved without a small portion of the salt being mechanically carried over, which cannot be a *desideratum* in an emollient.

By diluting with water the expressed glycerine, and shaking it with melted lard, and then allowing them to separate, an ointment may be obtained, which has the natural properties and aroma of the elder-flowers.

I will now draw your attention to what may probably be a very useful application of the above properties of glycerine,—I mean in cases where the aroma of the flower is so delicate

* Pure distilled glycerine has generally a specific gravity of about 1·260 at 60° F., but in ordinary glycerine may be concentrated upon a water bath until it has a specific gravity of 1·240.

as to be much injured, if not entirely destroyed, by the application of heat. When such is the case, the extraction of the perfume by glycerine may be substituted for the process of *enfleurage* as now carried on to such a large extent in the Var district of France.* The process would then become one of cold maceration, no heat being employed. After digesting the flowers for some considerable time in the glycerine, the latter is expressed and again treated with fresh flowers until the excipient is thoroughly saturated with the volatile oil; the extraction seems perfect, as the glycerine evidently has a great affinity for the odoriferous essences. (Fresh mint placed over a thin layer of glycerine imparts in a short time a considerable odor to that fluid, although it may not be in actual contact.) The saturated glycerine is diluted with water and shaken with a small quantity of chloroform; after well agitating, the latter is allowed to subside; it carries down with it nearly the whole of the essential oil. The chloroformic solution, after being separated by a funnel, should be filtered, if necessary, and allowed to evaporate spontaneously in a shallow vessel. The residual matter dissolved in spirit forms the spirituous extract of the flower, whatever that may be. If operating upon large quantities it becomes desirable to economize. Therefore, in such a case, the greater part of the chloroform may be drawn off in a still, the last portion being allowed to evaporate spontaneously; the boiling-point being so low that even the most delicate perfumes would hardly be deteriorated by the heat employed. Even the offensive smelling bisulphide of carbon, from its ready volatility, may be used; but it must be quite pure, or, in other words, it must be perfectly free from all after-smell on evaporation.

The glycerine may be used over and over again after diluting, passing it through charcoal, and then evaporating it to the desired gravity.

As regards the application of glycerine to the preserving of

* The commercial importance of this branch of trade may be indicated by the quantity of flowers annually grown in France, *i. e.* 2,284,000 lbs. This only includes orange, cassia, jasmine, and such like blossoms, the perfumes of which are extracted by the aid of fats. (*Vide* Exhibition Record, 1862.)

leaves, etc., for distilled waters, I have myself practically carried it out with great success, having kept flowers for two years, and on opening them, found not only the perfume natural, but the structure of the flowers without the least disorganization. The process proposed as a substitute for the ordinary one of *enfleurage* by fats, of course I merely throw out as a suggestion, as it could only be practically put to the proof at some place where the flowers are cultivated extensively. The great number of men and women employed in the present process at Grasse and Cannes would point out that a great saving would be made both in time and money by a method similar to the above. Another object is that although there are large growers at the above-named localities, the mass of the flowers are grown by cottagers, and collected from them by *commissionnaires*. In the glycerine plan the flowers could be placed in perfect safety as brought in, and by this means all danger from heating by fermentation is thrown out of consideration. I have extracted on the small scale, and by the above means, the aromata from *Heliotropium grandiflorum*, *Cheiranthus Cheiri*, and others. —*Pharm. Journ. and Trans.*, Nov. 1, 1864.

ON PREPARATIONS OF CINCHONA.

By Alfred B. Taylor.

"Is there an eligible means by which the medicinal matter of cinchona may be held in a permanent solution without deposition of cinchotannates or cinchonic red?"

In attempting to answer this query, I supposed the intent of it to be the finding a solvent which shall retain all the remedial properties of cinchona in their natural condition or combination, and without decomposition.

From the peculiar solvent properties of glycerin, it was thought that some combination of this substance with alcohol or sugar might answer the purpose, and accordingly the following experiments were instituted:

A tincture of cinchona was prepared, of the ordinary strength, using a menstruum composed of two parts of alcohol, one part of glycerin and one part of water. After standing for two or

three months there was no deposit from it, but the experiment (being only negative in its character) was not considered conclusive; since it does not follow that because after two months there is no precipitate, there will be none after a greater lapse of time. Recourse was had to another experiment; glycerin was added to the fluid extract of cinchona, prepared according to the U. S. Pharmacopœia, in the proportion of one part of glycerin to three parts of extract; upon heating this mixture it speedily became perfectly clear, much sooner than where the extract was heated alone; but upon cooling, the cinchonic red was thrown down and the mixture again became cloudy and opaque.

Another experiment was then tried, the quantity of glycerin being increased, and equal parts of glycerin and fluid extract being used. This mixture, after being heated as before, remained perfectly clear upon cooling. From this experiment it was thought that a fluid extract might be prepared with glycerin alone, which would satisfy the conditions of the query, and an extract was prepared by the following formula:

Take of Yellow Cinchona, in moderately fine powder, eight troyounces.

Glycerin } each eight fluidounces.
Alcohol }

Diluted Alcohol a sufficient quantity.

Mix the glycerin and the alcohol, moisten the cinchona with six fluidounces of the mixture, allow it to stand for half an hour, pack it firmly in a cylindrical glass percolator, and gradually pour upon it, first the remainder of the mixture and then diluted alcohol, until two pints of tincture have been obtained or the bark is exhausted; evaporate this to a pint by means of a gentle heat.

A sample of the extract, as thus prepared, is herewith submitted. It is beautifully clear, possesses all the remedial properties of cinchona in perfect solution, is not liable to change by fermentation, as is the fluid extract of the U. S. Pharmacopœia, and is believed to be in many respects superior to that preparation.

The success which attended this experiment naturally suggests the use of glycerin in the preparation of other apothemic extracts, more especially the astringent ones; (no doubt it would be useful in the preparation of fluid extract of rhubarb;) and it is believed that in the hands of future experimenters it will be found a most useful solvent in such preparations.

It was thought that the addition of acids, or perhaps of alkalies in small quantity, to the menstruum might render the tincture of cinchona a permanent solution, notwithstanding the fact that the character of the resulting preparation would be somewhat modified thereby. The addition of ammonia or potassa to the tincture of cinchona deepened its color, and by dissolving the cinchonic red, permanently prevented its deposition. Upon standing, however, minute crystals of cinchonia or quinia, or perhaps both, were deposited upon the sides and bottom of the bottle containing the tincture, and consequently the preparation was more injured than it would have been by the deposition of the cinchonic red, if the alkali had not been added.

The addition of an acid to the tincture of cinchona seems to render the solution almost, if not entirely, permanent; and, although in this experiment, as in the preceding one, the natural combination of the constituents of cinchona bark is not preserved, it is believed that an acidulated tincture of cinchona would, in very many cases, prove a valuable and desirable preparation.

The following formula is suggested for this preparation:

Acidulated Tincture of Cinchona.

Take of Yellow Cinchona, in moderately fine powder, six troyounces.
Aromatic Sulphuric Acid half a fluidounce.
Diluted Alcohol a sufficient quantity.

Having mixed the acid with a pint of diluted alcohol, moisten the powder with two fluidounces of the mixture, pack it firmly in a glass percolator, and pour upon it, first the remainder of the mixture, and afterwards sufficient diluted alcohol to make the tincture measure two pints.—*Proc. Amer. Pharm. Assoc.*, 1864.

ON THE ODOR OF COMMERCIAL TANNIC ACID.

By William Procter, Jr.

The following query was accepted by the writer:—"Pure tannic acid being an odorless substance, is there an odorous substance in nutgalls, that is found adhering to commercial tannic acid? or is the odor commonly noticed in that substance due to impure ether used in its preparation?"

According to Dr. Wood (U. S. Disp.) "galls are inodorous." Pereira says, "Galls have no odor." (Elements, page 323, vol. II. Am. Edit.) Christison also says, "Galls are without odor." Notwithstanding these opinions, at least two of these authorities give volatile oil as one of the ingredients of nutgalls.

My own examination of galls induces the opinion that, in their whole and dry condition, they have but little odor where they are in a box or drawer; when, however, galls are bruised, or in a powder, a distinct odor is manifest, which is well marked, though not very prominent. When, therefore, ordinary alcoholic ether is allowed to percolate powdered galls, it should remove this odorous substance along with the tannic acid and green and brown coloring matters, and deposit them on evaporation with any impurities the ether may contain.

To put this matter to a practical test, a bottle of ether was procured from Dr. Squibb, which left hardly a trace of odor when evaporated on a surface. This was mixed with a due proportion of alcohol and water, and passed through powdered galls. The ethereal percolate was evaporated to dryness in a capsule, with sufficient heat, until the ether was dissipated. The residue, when dry and brittle, was rubbed to powder. It had a greenish color, and a decided odor of bruised nutgalls, but no odor of impure ether.

A portion of this tannin was digested in benzine, in which liquid, tannic acid is insoluble, and on evaporating the benzine in a glass capsule, until the odor of that substance entirely disappeared, a minute residue, possessing the well marked odor of nutgalls, remained in the capsule.

The inference, therefore, is, that the odor of commercial tannic acid is chiefly due to the odorous principle of nutgalls, to which

is added the coloring matter of the galls, and sometimes odorous matter derived from the ether; and that, owing to the insolubility of tannin in benzine, its odor and some of its color may be removed by digestion with that liquid.—*Proc. Amer. Pharm. Assoc.*, 1864.

ON THE RANCIDITY OF FATS.

By Thomas B. Groves, F.C.S.

(*Read at the Bath Meeting of the British Pharmaceutical Conference, Sept.* 1864.)

Some experiments relative to the action of certain odorous principles in preserving the neutrality of fats, commenced in December, 1861, and not yet reported on, would, I thought, form the basis of a paper on the above interesting subject.

To the invalid who suffers from applying to an inflamed surface an irritant instead of emollient substance, as well as to the pharmaceutist who sustains pecuniary loss from the spoiling of his ointments by rancification, the question is doubtless important.

Rancidity may be defined as the changed condition, assumed sooner or later by all natural fats exposed to air and moisture, such change being characterized by loss of blandness and neutrality and development of pungency and acidity.

The cause of change being hidden, or at best imperfectly understood, the change has been termed spontaneous, or classed among those determined by catalytic influence. Chemically speaking, it consists in the separation of the neutral fats into its components, fatty acids and glycerin,—the latter substance almost invariably accompanied by obscure products of decomposition of an offensive and noxious character.

Palm oil is, I believe, the only fat that has been observed to separate *distinctly* into acid and glycerin.

It will throw much light on the nature of the change if we carefully watch its progress from the first appearance until the full development of rancidity.

That is done with most ease in ointments containing coloring matter of a vegetable origin, such as savine, or mineral, as oxide of mercury; but in pure lard it is not difficult.

The best chemical test of rancidity I find to be iodide of po-

tassium, which when mixed with fat in the least degree affected, quickly assumes an orange color, indicative of the presence of free iodine, the tint being directly proportional to the amount of rancidity. Thus I have found that when added to fat extremely rancid, the coloration is intense and immediate; when added to mixtures of this fat and other perfectly neutral, the coloration is less and less according to its dilution, and is plainly perceptible when the fat contains only one-twentieth, but a longer time is required for its development.

Acidity cannot be relied on as the index, for it will be found, that whereas the highly rancid fat, when boiled with alcohol, yields a solution reddening decidedly, though not promptly litmus-paper, a mixed fat, such as the above, gives a negative result.

When rancidity first shows itself in a pot of lard that has been filled with the melted fat and not subsequently disturbed, the following phenomena may be observed. Here and there throughout its contents, but more especially at the points where the lard touches the sides of the stoneware jar, small patches of a whiter and more crystalline aspect than the bulk have made their appearance. If these patches are tried by iodide of potassium, they will be found to be highly rancid, whilst the surrounding parts retain unimpaired their original freshness. As the process advances, these patches increase in size and number, until the whole mass has become infected. How far the action would proceed if time were given it is uncertain, but ordinary cases of rancidity are caused by the splitting up of a small portion only of the fat. From the change taking place in situations to which the air cannot be supposed to penetrate,—for instance, the interior of a homogeneous mass of fat,—it may be inferred that air is not necessary to its *propagation*. Analogy coupled with the observation that rancidity first makes its appearance at the sides of the vessel, where possibly from contraction during cooling a small air-space may have been left, point to the necessity of air being present at its *commencement*. In fact, it is pretty sure that the phenomena are caused by a species of fermentation involving the joint action of air, water, albuminous matter, and a moderate degree of heat. Such is the opinion of M. Pelouze, who has written much on the ques-

tion, and of whose valuable labors I have freely availed myself.

There can be no question of the presence of water in all neutral fats; albuminous matter in some form may also be safely assumed to be in company with it. It is often met with in a flocculent form at the bottom of jars of olive oil, and cannot fail to be present in all fats of animal origin, whilst MM. Saussure and Pelouze have noted the absorption of oxygen during the drying of siccative oils, some of which in return evolve hydrogen and carbonic acid. I have myself observed a candle lowered into a jar partly filled with cod-liver oil, that had remained some time in contact with the air in the upper part of the vessel, suddenly extinguished. It is doubtless true, on the supposition of a ferment being the agent that effects the disturbance, that the removal of any one of the essential conditions would prevent its action. But can it be done in a practical way? I believe not. To remove the last trace of *humidity* would be impossible, except by tedious and expensive methods. Still, a partial drying is better than none, and the experience of housewives is unanimous on the point as regards the melting of lard, which they say will not keep unless it has been made to boil. *Albumen* has been sought to be removed by agitation with sulphuric acid of 40° Beaumé, washing with water and subsequently drying. The process was employed some years ago in preparing rape oil for burning in light-houses, and was found to hinder its oxidation. I have not been able to imagine an *easy* process for freeing oils, etc., of this dangerous ingredient, and have, therefore, made no experiments in that direction. M. Pelouze made many attempts to insulate the body, but failed. Nevertheless he was able from its effects to identify it as one of the albuminous series. I shall be able to show, further on, that its activity may be effectually neutralized by a simple method. The entire exclusion of *air* is of course practically impossible.

The length of time required for the development of these changes makes experimenting very tedious, and renders one unable to do so much in a given time as one could wish. I have, therefore, confined myself within very narrow limits, relating to practical remedies only, and to lard as the base of experiment.

Shortly after the use of benzoinated lard had been recommended for the preparation of zinc ointment, which it is well known to preserve against rancification, I applied with success the same idea to other ointments of similar composition, viz.: those containing metallic oxides, whose presence had been found to act unfavorably on the keeping qualities of the fats with which they were associated. These were calamine cerate and oxide of mercury ointment. I have found that M. Deschamps, in 1843, recommended the same proceedings in making oxide of mercury ointment, and also the ointments of iodide of potassium and acetate of lead. For ointment of tutty and blue ointment, where a little extra color would not be objectionable, he directs the use of "graisse populinée, the keeping qualities of which are really extraordinary. M. Deschamps states that whilst the "graisse benzinée" will keep good for one year, the "graisse populinée" will keep good for an unlimited time. He suggests its use for greasing machinery even. I intended to make some of this preparation, but could not get the poplar buds. The French perfumers, in preparing the base of their pomades, adopt a process somewhat similar, viz., digestion with benzoin after a preliminary washing, and boiling with solution of salt and alum. Their method yields a stable fat, but it is too troublesome to be be frequently performed, and succeeds best on the large scale,—consequently is not well adapted for the pharmaceutist.

For experiment on the nature of the preservative power exercised on fats by bodies like benzoin, the oxide of mercury ointment was evidently well adapted, as the progress of rancification is marked by alteration of color—the oxide being reduced *pari passu* with the oxidation of the fat.

It was my impression that the essential oil had more to do in the matter than any other constituent of the gum, though it had been asserted that benzoic acid answered equally well. But the acid of commerce contains an abundance of the odorous principle.

To test the truth of the surmise, and at the same time ascertain what degree of effect, if any, was produced by various essential oils, I prepared, on December 5th, 1861, a quantity of red precipitate ointment, using ordinary lard and wax in the

prescribed proportions, and a smaller quantity using benzoinated lard. To small portions of the former I added essential oils, in the proportion of four drops to the ounce. The oils I used were fennel, almond, bergamotte, cassia, turpentine, lavender, neroli, lemon, rose, rosemary, caraway, nutmeg, savine, pimento, cumin, clove and sassafras. I also tried creasote, balsam of Peru, Venice turpentine, and powdered guaiacum. These were all put into willow boxes, and, in order to hasten the reaction, placed in a warm situation, whose temperature ranged between 70° and 80°.

On the 28th of the following February (85 days), I observed the ointment made with plain lard to be slightly discolored. By the 11th of March (96 days), the change had developed itself in the lavender, neroli, lemon, rosemary and caraway, which, with the plain, *were most discolored.* Next came cassia, Venice turpentine, less discolored, and then fennel, almond, and bergamotte, least discolored. In some cases the interior was more discolored than the exterior. April 19th, 1862, (135 days), the most changed were the plain and bergamotte; the next best, cassia, lemon, rosemary, lavender, almond, and turpentine; the least changed, neroli, Venice turpentine, fennel, and caraway. The rest continued good. On the 2d of June (179 days), the only kinds remaining undiscolored were rose, pimento, clove, creasote, cumin, sassafras, guaiacum, and balsam of Peru, the least affected of the remainder being benzoin, which now had given way.

By the 10th of September, (279 days), rose and cumin had become discolored, leaving good only clove, pimento, Peruvian balsam, sassafras, guaiacum, and creasote, all of which at the present date are apparently as good as ever.

December 5th of the following year (1862), I put by, under the same circumstances, another series of ointments containing four drops to the ounce, and a second series containing only two drops to the ounce of the following oils, etc.:—Clove, sassafras, pimento, balsam of Peru, and creasote,—those, in fact, that had comported themselves best on the prior occasion.

By May 5th, 1862 (151 days), the plain ointment was spoiled. By August 11th, 1862 (249 days), the benzoinated and No. 2, sassafras. At the present date (August 29th, 1864), balsam of

Peru No. 2 shows symptoms of giving way, but all the rest are apparently as good as ever. In order to ascertain the actual condition of the fats—to try whether or not the test of color could be relied on—I recovered them by means of benzole from the No. 2 creasote and No. 2 pimento, and found them react perfectly neutral with iodide of potassium, notwithstanding they had been purposely kept under the most unfavorable conditions for upwards of twenty months.

The action of creasote, the great antiseptic, is not difficult to understand; but whether the essential oils shared its power to prevent the putrefaction of albumen remained to be proved. To do so, I prepared a filtered solution of egg albumen, and to 2-ounce portions of it, placed in 3-ounce bottles, I added two drops of each of the essential oils I had used with the ointments, dissolved in ½ drachm of rectified spirit. One portion, mixed with spirit only, was placed with them for comparison. They all were set aside in the situation previously occupied by the ointments. The unscented albumen became putrid in twenty-eight days; the other specimens are still good. I expect them to observe the same order in this experiment as in those with the ointments. I may add, that all these essential oils precipitate albumen, some more, some less.

Having succeeded so well with the ointment of oxide of mercury, I commenced, January 22d of this year, to try similar experiments on pure lard.

Twelve pounds of fresh flare were completely deprived of flesh and membrane, bruised well, washed under a stream of water, and placed in a porcelain vessel over a water-bath. As soon as one-third was liquefied, that portion was strained and set aside. The temperature had not exceeded 140°. This lard I shall refer to as No. 1.

The rest was kept on the bath one hour after total liquefaction, then strained, its temperature being 190°; half of it was set aside = No. 2.

The remainder was gradually heated to 220°, and kept at that temperature for five minutes = No. 3. It was much firmer than either of the preceding, and maintained that distinction after being stirred.

Of each of these lards I set aside, in willow boxes, three

specimens, viz.: lard well stirred, lard mixed with oil of pimento in the proportion of two drops to the ounce, lard mixed with oxide of mercury one drachm to the ounce,—and placed them where the temperature ranged between 70° and 80°.

On the 21st of April (ninety days) I first observed a change in the lards mixed with oxide of mercury,—No. 1, strained at 140°, being the least, and No. 3, strained at 220° the most altered. The scented and plain lards, tested with iodide of potassium, all produced slight coloration after half an hour, but the scented lards less than the plain. No. 3 appeared to better advantage than the less heated specimens. After thirty hours' exposal on the slab to light and air, a most extraordinary change was observed. Nos. 1 and 2 of the plain lards had assumed an orange color, No. 3 a similar tint, but only half as dark, whilst the scented lards had lost rather than acquired color,—in fact produced an ointment at that time perfectly saleable. The contrast was most striking, and continued so for two months; by which time *all* the specimens were of an orange color, but the scented lards only *externally*,—probably affected by the fumes of the laboratory.

These same lards were again examined July 7. Those mixed with oxide of mercury were all hopelessly bad. The rest were tested with iodide of potassium, and after eight hours' exposure presented the following appearances:—Nos. 1, 2, and 3 of the plain were of a lemon color, the tint of No. 1 being less than that of No 2.; of No. 2 less No. 3. The scented lards still maintained their superiority, Nos. 1 and 3 being quite useable, No. 2 not so.

August 26th, I again examined them, with the same results.

I therefore conclude that oil of pimento, which, of those that had maintained the neutrality of oxide of mercury ointment, appears the best adapted for the purpose, is a useful, agreeable and easily applied remedy for preventing or very much retarding rancification in fats and fatty mixtures.

I think I am also justified in adding this corollary—that it is advisable when preparing ointments with a view to their preservation, to use ingredients retaining unaltered the odorous principles with which nature has for obvious purposes endowed them; that is to say, I would use yellow wax instead of white

wax, yellow olive oil instead of bleached olive oil. In fact, experiment has shown the superiority of these bodies not meretriciously tampered with, over the same bodies to which a false appearance of excellence had been given by exposure to bleaching agents, no matter how simple and apparently harmless their nature.

The experiments on the effect of temperature I have repeated more than once. They go to prove that it is not advisable to push the heat beyond that of the water bath, nor maintain it too long at that temperature. I say this feelingly, as the undecisiveness of my first experiment and a certain amount of belief in the old wives' tale about *boiling* lard, induced me to try the superheating process on a large scale,—and most unfortunate was the result.

I consider the British Pharmacopœia process, where the flare is melted by water-bath, the fat strained from the membrane as soon as possible, and then dried by water-bath, to be an excellent one. I would only suggest the advisability of adding to it oil of pimento or balsam of Peru, in the proportion of two drops to the ounce, before placing it in stock. Such addition does not in any way interfere with its medicinal use, and would as I have shown, much conduce to its preservation.—*Lond. Pharm. Jour., Nov.*, 1864.

ON THE PHARMACEUTICAL APPLICATIONS OF GLYCERINE.

By Mr. F. Baden Benger.

Read at the Bath Meeting of the British Pharmaceutical Conference, Sept. 1864.

The Edinburgh branch of the Pharmaceutical Society thought proper to award me the President's Prize for an essay on this subject a few months since, and it is from that paper chiefly that I have taken the following notes. It is needless to detain the Members of the Conference by giving a detailed account of the introduction of glycerine into pharmacy, nevertheless I should like to make a few remarks on this part of the subject. Glycerine, as is well known, was discovered by Scheele; but I find considerable discrepancy in the ascribed dates. Watts, in

his "Chemical Technology," gives 1776; Demarquay, in his recently-published treatise "De la Glycérine," Gerhardt, and others, 1779; M. Chevalier, in reporting on a paper by M. Bruere Perrin in the "Journal de Chimie Médicale," 1782–83; while Dr. Abbotts Smith and others make it as late as 1789; but the fact that Scheele published his discovery in the "Transactions of the Royal Academy of Sweden" in 1783, seems to prove the latter date erroneous. It is to M. Chevreul, however, that we are indebted for giving to this substance "a local habitation and a name," which he accomplished about thirty years after its discovery, by demonstrating the true part it played in the constitution of fatty bodies (viz., that of a base, combined with stearic, margaric, and oleic acids). He gave it the name of glycerine, it having been previously known as the "sweet principle of oils." In 1844 it was first used in England as a therapeutic agent, but attracted little attention till the publication of the admirable papers of M. Cap, in the "Journal de Pharmacie et de Chimie" for February, 1854, and MM. Cap and Garot in the same Journal, August, 1854. These gentlemen pointed out the peculiar advantages offered by glycerine as a solvent, and, by a very complete course of experiments, suggested for it almost innumerable pharmaceutical applications. They devised means of obtaining it in a much greater state of purity from the waste liquors of the soap-boiler than it had hitherto been supplied, but it was found impossible to rid it entirely of the impurities (especially volatile fatty acids) derived from the substances used in the manufacture of the soap. The purest glycerine was at this time obtained during the process of making lead plaster. A very important discovery was made by Mr. Richard Albert Tilghman, of Philadelphia, about this date, viz., the possibility of separating glycerine from fats by the aid of heat and water only. A patent was granted to this gentleman January 9th, 1854. In his specification Mr. Tilghman says, "I subject these fatty or oily bodies to the action of water at a high temperature under pressure, so as to cause the elements of these bodies to combine with water, and to obtain, at the same time, free fat acids, and solution of glycerine." The temperature used by Mr. Tilghman was that of melted lead (612° F.). Great improvements in the details of this process were shortly after-

wards made by Mr. G. F. Wilson, F. R. S., of the firm of Price and Co., Vauxhall. As a source of glycerine he employs palm-oil bleached by exposure to the air; this is decomposed in suitable apparatus by steam at a temperature of 550° to 600° F., maintained for several hours. The glycerine is then allowed to distil over with the fat acids and water, and is concentrated by evaporation. Price's glycerine is well known at home and abroad for its great superiority and almost absolute purity, being of necessity free from inorganic matter. For, as Mr. Wilson has himself said, "The only chemical agents used for decomposing the neutral fat, and separating its glycerine, are steam and heat, and the only agents used in purifying the glycerine thus obtained, are heat and steam." Mr. Wilson tells me that they are now making one ton per week of this pure medicinal glycerine, and, in order to ensure its perfect purity, it is frequently distilled five or six times. Like Bennett's watches, Price's glycerine leaves "nothing to be desired but the money wherewith to buy it."

It is in external remedies that the greatest field appears to be open for the further introduction of this substance in pharmacy, and I shall first call attention to the compound of starch and glycerine known as "plasma." It had long been thought desirable to find a substitute for fatty matters in ointments not liable to become rancid, and in 1858 Mr. Schacht, of Clifton, read a paper before the Pharmaceutical Society, in which he proposed for that purpose a mixture of seventy grains of starch with one ounce of glycerine, heated together to a temperature of 240° F. The product is a plastic mass well suited in most respects for the purpose, but has been objected to from its tendency to absorb moisture and become fluid by long exposure to the atmosphere. The inconvenience arising from this source, however, might be easily obviated by keeping the plasma in air-tight jars, and dispensing it when necessary in wide-mouthed bottles. A much more serious hindrance to its general use is the fact that it costs about five times as much as the ordinary adipose basis of ointments.

I have made a variety of experiments with "plasma," substituting in its composition for the common wheat starch that of arrow-root, rice, potato, tous-les-mois, etc., all of which yield

compounds differing from each other in some of their physical properties. The arrow-root plasma is beautifully transparent, but has an objectionable tenacity if more than sixteen grains to the ounce be used. On the whole, I prefer the tous-les-mois preparation to any other. The best mode of preparing this is, to rub together in a mortar fifty grains of tous-les-mois with one ounce of glycerine; transfer this to a porcelain evaporating-dish, and heat over a gas flame to a temperature of 240°, constantly stirring with an ivory or wooden spatula. (A prescription recently came under my notice, in which an eminent surgeon had ordered starch and glycerine to be heated to this temperature over a water-bath!!) Some pharmaceutists recommend that the plasma should be kept at 240° for twenty minutes, but I see no advantages likely to accrue from this, and unless great care be taken to regulate the temperature the compound will become colored, and will always be found to have diminished considerably in weight, a result not at all satisfactory to the operator. If the application of heat be continued only long enough to burst the starch granules, or till the mixture becomes transparent, the loss will be about twenty grains to the ounce. The presence of a little water is not detrimental; indeed, I believe it improves the condition of the product, as it will be found more plastic and better suited for rubbing over the surface of the skin, even after it has been exposed to the air a few weeks, and thus absorbed more moisture. M. Surum, a French pharmaceutist, who has paid much attention to the subject, advises ten per cent. of water to be added to the starch previous to mixing it with the glycerine. I do not think plasma would be advantageously substituted for fats in all ointments, but in those cases where there is a great tendency to rancidity, as in the Cer. Calam., Cer. Plumbi Acet., Ung. Zinci, etc., of the old Pharmacopœia, and where the active ingredient of the ointment is soluble in glycerine, as in the Ung. Potass. Iod., Ung. Aconitiæ, Ung. Atropiæ, Ung. Belladonnæ, Ung. Creosoti, and Ung. Veratriæ of the British Pharmacopœia, the plasmas appear preferable to the analogous ointments; it also has the advantage of being easily removed from the skin without the aid of soap or friction.

Those preparations in which glycerine alone is the basis have

received the name of glyceroles. Many substances are more soluble in glycerine than in water or alcohol. When an aqueous or spirituous solution is applied to the skin it rapidly becomes dry; and it seems reasonable to suppose that absorption would then be greatly retarded. Glycerine is free from this objection, and its peculiar power of penetrating the pores of the skin renders it the best menstruum for many substances. Dr. Richter, of Vienna, proposed, in 1857, a caustic application, composed of one part of iodine, two of iodide of potassium, and two of glycerine. I am surprised that this in various states of dilution has not been more frequently used instead of the tincture. Glycerine dissolves five grains of iodine to the ounce without the addition of iodide of potassium. A glycerole, composed of tannin one part, glycerine four parts, is a very elegant preparation, and is used as an application to the throat, etc., *per se*, and as an addition to gargles, lotions, injections, etc. One ounce of glycerine dissolves fifteen grains of atropia, and seems to offer some advantages over solutions containing acids in combination with the alkaloid in ophthalmic surgery. Borax is soluble in glycerine to the extent of fifty per cent., and by adding this solution to tincture of myrrh, we obtain a "tincture of myrrh with borax" superior to that prepared in the ordinary manner. The non-resinous vegetable extracts are soluble in glycerine,—a solution of the alcoholic extract of Calabar bean has lately been used with success.

In the other class of medicaments, viz., internal remedies, the use of glycerine has hitherto been more limited. Although glyceroles have often been brought before our notice as substitutes for syrups, I do not find that they generally possess any superiority. I have prepared the glycerole of iodide of iron in two ways:—first, by making a very concentrated solution of iodide of iron (about equal weights of water and iodine with iron wire, q. s.) and filtering this solution into glycerine; and, secondly, by a process suggested by Mr. James C. Leamy, of America, in 1848, viz., to make a more dilute solution of the iodide, mix with the glycerine, and evaporate the water over a water-bath. The former is nearly colorless, but remains so only for a few days. The latter is of a pale straw color, and appears much less liable to undergo further change. A glycerole of carbonate

of iron may be made by dissolving separately, each in 2 ounces of glycerine, 76 grains of sulphate of iron and about 60 grains of carbonate of potash, and mixing the solutions. The result will be a pale-green solution of carbonate of iron, containing 1 gr. in fʒi., which will keep a considerable time without change. The carbonate of iron is thrown down as a flocculent precipitate on the addition of water. Gum Ammoniacum forms a white creamy emulsion with glycerine, in the proportion of ʒi. to fʒi., which, according to Demarquay, does not separate. I imagined this might be useful for the instantaneous production of a kind of Mist. Ammoniaci, but the result of my experience is that the resinous part of the Ammoniacum gradually separates and rises to the surface, leaving an opalescent solution of the gummy constituents below. There is one other use for glycerine which must not be overlooked,—that of an excipient in pill-masses. Alone or diluted with an equal weight of water it is decidedly the best thing for "making up" pepsine and vegetable powders, care being taken not to add too much, and to thoroughly knead the mass. Pills made with this do not become hard, and are therefore always in a condition to be readily dissolved in the stomach. A two-ounce wide-mouthed bottle fitted with a cork perforated in two places, through one of which a piece of quill is inserted for dropping the glycerine from, will be found a very serviceable adjunct to the dispenser's board.

Glycerine has been honored with a place in the British Pharmacopœia, where, however, it has only been thought worthy of acting as a solvent for the tannin in "Suppositoria Tannici." The test there given is that it shall have a density of 1·26 (the new Pharmacopœia of the United States gives 1·25). Price's is almost the only sample I have met with which reaches this standard, the specimens of foreign glycerines I have examined being considerably below the mark, and, with one exception, having a disagreeable odor. This odor may easily be detected by rubbing a few drops on the back of the hand. One of the worst of these importations was advertised as "equal to Price's in every respect." I have not detected much inorganic impurities in the foreign glycerines, and the presence of water would be of comparatively little import, if it were possible to free them from the well-known rancid odor, which renders them totally

unfit for pharmaceutical uses. The olfactory nerves of that man must indeed be torpid, who fails to discover a wide difference between Price's and the cheaper glycerines. Should odor, however, not be sufficient proof, let a little solution of nitrate of silver be added to the specimen in a test tube and exposed to the light; Price's will be found to remain nearly colorless, whilst the inferior samples will rapidly become dark-colored. When we are able to obtain Price's glycerine, or glycerine equal to it in every respect, at 1*s.* 6*d.* per pound, I have no doubt but it will find many applications in pharmacy from which it is now debarred by its great cost.—*London Pharm. Jour., Nov.*, 1864.

ON THE MORPHIA SALTS OF COMMERCE.

By W. E. Heathfield, F. R. G. S.

(*Read at the Bath Meeting of the British Pharmaceutical Conference, Sept.*, 1864.)

Amongst the many vegetable products from which are obtained the alkaloïdal bodies, there are none, as at present known, of so complex a character as opium; none which yield so largely their crystalline formations, and none which afford so many substances, each presenting a different feature and a different habit.

Of these substances, amounting to about eleven, six have been carefully analysed, and the verifications of the results by Professor Anderson, of Glasgow, together with the experimental performances upon some of them by Mr. How, have contributed much to render this part of the subject complete. The subjoined list indicates the six bodies to which I refer, and the composition of each:—

Morphia	$C_{34}H_{19}NO_6 + 2$ aq.
Codeia	$C_{36}H_{21}NO_6$ "
Thebaina	$C_{38}H_{21}NO_6$ "
Papaverina	$C_{40}H_{21}NO_8$ "
Narcotina	$C_{46}H_{25}NO_{14}$ "
Narcein	$C_{46}H_{29}NO_{18}$ "

And it is to be observed that the two first-named, *i. e.* morphia and codeia, differ from each other exactly by C_2H_2, and it suggested itself to Mr. How (whose experiments were tried in the year 1853, as detailed in the 'Journal of the Chemical Society,'

vol. vi. p. 125, May, 1854), that morphia might be converted into codeia by the decomposition of an agent ready to part with the elements in question, and so produce the proposed effect.

But easy as the transition of morphia into codeia appears, on a comparison of their respective rational formulæ, the object was not attained by Mr. How, who came to the conclusion, that by any means at present within our reach, no great stimulus is afforded to us to prosecute inquiries for the production of this or other of the natural alkaloids. It is true that Mr. How obtained, by means of iodide of ethyl acting on morphia, a salt isomeric with hydriodate of codeia, but beyond isomerism it was in no way identical with it, for the base of the new salt was widely different in its physical and chemical properties from codeia. Yet it has been thought by some eminent manufacturers of morphia and codeia, that there is a tendency on the part of the former to change into codeia under the influence of certain agencies, and it would be an interesting feature if this point could be established.

In following out some experiments, having in view the state of hydration, and the freedom from codeia of the morphia salts of commerce, I endeavored, after examining samples from various sources, to confine myself more especially to those of different manufacturers, and I propose to report upon three specimens, each being of different make. Of each specimen 100 grains (of hydrochlorate of morphia) were dried at a temperature of 212°.

No. 1.	100 grains.	Weight after drying,	95 grains : loss, 5 grains.
No. 2.	100 grains.	" "	92 grains : loss, 8 grains.
No. 3.	100 grains.	" "	90·2 grains : loss, 9·8 grains.

The characteristics of solubility were as follows :—

No. 1, immediately on contact with water, became dark in color, and united to form a clot, taking some minutes to dissolve, and then forming a solution somewhat colored.

No. 2, on contact with water, became very slightly colored, formed but little clot, and dissolved in less time considerably than the former, producing a solution slightly tinted.

No. 3, not at all darkened on contact with water, remained pulverent, and separate, and dissolved with rapidity, forming a perfectly colorless solution.

On precipitating a solution of 100 grains of hydrochlorate of morphia from each of the three specimens, the results were as follows:—

No. 1. Precipitate, colored yellow, and pulverent (dried at 212°) 79·7.
No. 2. Pearly white, crystalline . . . . . 76.7.
No. 3. Less white, less crystalline . . . . . 74·3.

These precipitates were entirely soluble in a solution of caustic potash; and were scarcely acted upon by anhydrous ether.

100 grains of acetate of morphia from each of three specimens were subjected to a temperature of 212°, and lost as follows:—

No. 1. 100 grains. Weight after drying, 95 grains: loss, 5 grains.
No. 2. 100 grains. " " 90 grains; loss, 10 grains.
No. 3. 100 grains. " " 87·4 grains: loss, 12·6.

No. 1, on applying the heat of water bath, became dark-colored, fused into a colored mass, and finally lost its structure.

No. 2 on applying a similar heat, became partially fused and dark-colored, but scarcely lost its structure.

No. 3, retained its pulverent form throughout the process.

On an examination being made of the precipitates by ammonia from the hydrochlorate of morphia, they proved to be morphia in a high degree of purity, perfectly soluble in caustic potash, scarcely acted upon by ether, and almost entirely free from codeia, as was also the mother-liquor from which they had been precipitated.

On a review of these experiments, it will be observed that the three samples of hydrochlorate of morphia contained varying proportions of water, and varying quantities of the alkaloid in like proportion,—that which was the least soluble, No. 1, having the largest proportion of the alkaloid; that which was most so, containing the largest proportion of water, as in No. 3; the difference between No. 1 and No. 3 being equal to nearly five per cent. of water, and nearly five and a half per cent. of alkaloid. The codeia appeared in each specimen to have been carefully separated. The range of moisture in the acetate was a little wider than in the hydrochlorate, the loss in No. 1 being five per cent., whilst that in No. 3 was about twelve and a half per cent.

I regret that I have not been able to carry out this investigation

to the extent that I had proposed and wished, but should I be again permitted to furnish a paper to the Conference, I hope to devote more attention, and to direct my observations more usefully. —*London Pharm. Jour., Nov.*, 1864.

EXPERIMENTAL RESEARCHES ON OPIUM AND ITS ALKALOIDS.

By M. Claude Bernard.

This eminent physiologist was led to experiment on the effects of all the alkaloids of opium from noticing great and unexpected variations in those effects when the alkaloids were employed to facilitate experiments on living animals. He found, in fact, that the six principal alkaloids—morphia, narceia, codeia, narcotina, papaverina and thebaina—each produced a particular effect, but the action may be classed under three heads—the soporific, the exciting or convulsive, and the poisonous action. The relative power of the alkaloids to produce these effects is indicated by their position in the following table:—

Soporifics.	Excitants.	Poisons.
Narceia	Thebaina	Thebaina
Morphia	Papaverina	Codeia
Codeia	Narcotina	Papaverina
	Codeia	Narceia
	Morphia	Morphia
	Narceia	Narcotina

Thus it is seen that three only produce purely soporific effects, but even these vary greatly in character and degree. Morphia, for example, produces a stupifying effect. The animal is scarcely insensible, but becomes a sort of living machine, and will remain in any position in which it is placed. The sensitive nerves are extremely dull, and the extremities may be strongly pinched without disturbing the animal. When roused by a noise it seems frightened, but quickly relapses into narcotism. As the animal awakens it has a haggard look, and the hinder extremities seem partially paralysed, so that it walks like a hyæna.

The effects of codeia are essentially different. The animal is tranquil, and seems to be in calm sleep, but he is at the same time very excitable; a slight noise wakes him up, and he runs

away. The sensitive nerves are much less affected than by morphia, and no paralysis is observed when the animal awakens.

Narceia seems to produce the combined effects of morphia and codeia, and appears to be the most strongly soporific principle in opium. The animal sleeps more profoundly, but is not so much stupified as with morphia; and at the same time is not so excitable as when under the influence of codeia. It quickly returns to its natural state, and on awaking is neither frightened nor savage.

All these effects have been confirmed by repeated experiments on all available animals, and they appear to be constant and invariable.

Coming to the poisonous effects of the alkaloids, the author informs us that thebaina is the most active poison. A decigramme of the hydrochlorate of this alkaloid injected into the veins of a dog killed it in five minutes; but it is stated that *two grammes* of hydrochlorate of morphia injected into the veins of a dog of the same size did not cause death. There must, we think, be some mistake here; *two decigrammes*, perhaps, are meant. Codeia stands intermediate as a poison.

Thebaina also stands first as the most powerful agent in producing convulsions.

The inquiry which M. Bernard has thus opened is very large and important, and will, no doubt, be followed out with all the skill and care for which he is distinguished.—*Comptes Rendus*, and *Chem. News*, Sept. 10, 1864.

EROSION OF LEAD BY INSECTS.

A letter to the *Times*, signed "Y," states that the erosion of lead by certain species of insects is not generally known, and may be extremely mischievous. Not long ago it attracted the attention of the French Academy of Sciences, and several communications upon it have been published in their proceedings, the *Comptes Rendus*. In 1858 Marshal Vaillant exhibited to the Academy leaden bullets brought back from the Crimea, in some of which the larvæ of insects had excavated circular passages three or four millimetres in diameter; but nothing of the kind had been detected in the cartridges of the Russian army

in the Crimea, and the insect which damaged the French cartridges appears to have been imported in the wood of the cases in which they were packed. The insects do not eat the lead, but simply bore it out. In 1833 Audouin exhibited to the Entomological Society of Paris sheet lead from the roof of a building deeply grooved by insects. In 1844 Desmarest mentioned erosions of sheet lead by a species of Bostriche (*B. Capucina*), and illustrated the fact by cartridges from the arsenal at Turin. Mr. Westwood, the well-known British entomologist, has recorded observations on the perforation of lead by insects. M. Bouteille, curator of the Museum of Natural History at Grenoble, sent to the French Academy of Sciences from the collection under his charge specimens of cartridges gnawed by insects, which were found *in situ*, and the reports on the subject by Marshal Vaillant, de Quartrefages, and Milne Edwards, state the insect to be *Sirex gigas* a large hymenopterous species, which, in the larva state, lives in the interior of old trees or pieces of wood, and which, after the completion of its metamorphosis, quits its retreat for the purpose of reproduction. Scheurer-Kestner, in 1861, communicated to the French Academy a notice of the erosion by an insect of the sheet lead of a new sulphuric acid chamber. The creature was caught in the act of escaping through the lead, having been imprisoned between it and a wooden support. But perhaps the most interesting and important case of insect erosion is that of stereotype metal, which was communicated in 1843 by M. du Boys to the Agricultural Society of Limoges.—*Chem. News, Oct.* 1, 1864.

THE PREPARATION OF MATCHES FREE FROM PHOSPHORUS.

Hierpe has published* the following receipts for a composition for the heads of matches, and for an igniting surface. That for the matches is as under:

Chlorate of potash	. . .	4 to 6 parts.
Bichromate of potash	. . .	2 "
Ferric oxide	. . . .	2 "
Strong glue	. . . .	3 "

* *Polytech. Centralblatt*, 1864, p. 696.

Oxide of iron may be replaced by oxide of lead or of manganese. The above preparation will not ignite on sandpaper, but requires a surface specially prepared for it, and the author employs the following on the boxes:

Sulphide of antimony . . .	20	parts.
Bichromate of potash . . .	2 to 4	"
Oxide of iron, lead, or manganese .	4 to 6	"
Glass powder	2	"
Strong glue or gum . . .	2 to 3	"

Another composition is described by Dr. H. Poltzer.* A solution of sulphate of copper is divided into two equal parts—one is supersaturated with ammonia, the other with hyposulphite of soda. The two solutions are now mixed, and the mixture is briskly stirred. A violet-colored powder now deposits, which is a compound, says the author, of hyposulphurous acid with oxide and suboxide of copper, soda, and ammonia. A mixture of this salt with chlorate of potash detonates when struck with a hammer, and when rubbed in a mortar ignites and burns like gunpowder, leaving a black residue.

The above salt the author proposes to use for matches. It is not soluble in water, and the mixture with chlorate of potash is not hygroscopic. The mixture may be made with moist chlorate and the gum solution, and can be safely dried at 50° C. or higher. It inflames when rubbed on a rough surface, and the temperature developed is sufficiently high to ignite sulphur on the stick.

The only difficulty the author finds is in making the mass coherent: when dried on the stick he found that it would crack and drop off when rubbed. A manufacturer will probably soon overcome this difficulty.

The proportions made use of were one part of the copper salt, and two parts of chlorate mixed in a sieve, and then made into a mass with solution of gum, together with a little glass powder. This mixture was applied to matches dipped in sulphur as usual.—*London Chem. News, Dec.* 10, 1864.

* *Polytech. Centralblatt*, 1863, p. 1642.

Editorial Department.

British Pharmaceutical Conference.—In our last number reference was made to the meeting of this body at Bath, England, September last. The Pharmaceutical Journal of November contains the scientific papers read on that occasion, which have swollen the Journal to double its usual size. Some of these papers will be found in this number; that of Mr. Groves on the rancidity of fats, and that of Mr. Stoddart on the purity of sulphate of quinia, deserve attention. We hope in future numbers to reprint several others. Among those read that attracted most attention was that on Weights and Measures used in Pharmacy, by Barnard S. Proctor, who, for some years past, has given attention to metrology. In the course of his remarks on the various propositions which have been brought forward, this gentleman takes occasion to speak of Mr. Alfred B. Taylor's monograph on the same subject, published in the Proceedings of the American Pharmaceutical Association of 1859, in which he brings forward a new octonary system, embracing every form of measurement, in the following terms:—

"The proposition of the American Pharmaceutical Association, unquestionably the most carefully considered, the most elaborate, and most ambitious of the proposed plans, is based on the belief, and, I think, I may say, the well-grounded belief, that for all practical purposes counting by eights has the greatest sum of advantages."

We believe "the Conference" is really a success, and that its future promises well. The quality of the papers it has produced justify their publication in a separate form, and it is to be hoped that the proceedings of the next meeting will not only be issued in a separate and distinct volume,—the first of a long series,—but that, dropping the modest and initiatory title of "Conference," this body will adopt some such name as "British Pharmaceutical Association," representing as it should, and probably to some extent now does, every pharmaceutical interest and society.

Our School of Pharmacy.—It is a source of satisfaction that our College is rapidly recovering from the depressing influence exerted on scientific schools generally by the great Rebellion, and promises soon to regain its previous numbers. We append, as usual in our January number, a list of the Class and Preceptors, which this season reaches 106.

The Pharmaceutical Department of the Army.—We have for some time past entertained the idea of publishing in this Journal a record of the prominent facts connected with this branch of the medical service of

the army, and have taken some steps towards its accomplishment. In view of this we should be glad to receive any information bearing upon the subject in their department from the numerous graduates of Pharmacy, who now occupy positions as hospital stewards, medical storekeepers, or any others, where opportunity is afforded to acquire correct information. The idea is, to learn the general plan of conducting the field and hospital service, the amount of accuracy in the measurement of medicines observed in practice in the two branches of the service, and any legitimate information in reference to the general duties of pharmaceutists in the army. Also, information in regard to the amount of supplies actually consumed, compared with the amount issued from the public stores and laboratories, and the several amounts of production in these. It is altogether certain, that no such gigantic military pharmaceutical operations have ever been carried on in Europe, as the past three years have witnessed in the supply of the armies of the United States, and we deem it desirable to obtain and preserve a record of the facts as it is proper and right to publish them.

Poisoning by Belladonna Berries.—In a communication received from Henry F. Geyer, of Mechanicsburg, Pa., dated Dec. 11th, 1863, (and which was accidentally mislaid,) he sends the following slip from the *Cumberland Valley Journal* of the 3d of December, 1863, viz.:

"Sad Occurrence.—On Sunday night last, Alfred Cookman, an interesting little son of Mr. Benjamin Haverstick, of this place, aged about eight years, died under the following melancholy circumstances: On Friday afternoon, while playing in the vicinity of Mr. Troutwine's garden, in Locust street, he came to a stalk of Nightshade, and, not knowing what it was, ate some of the berries. On the following morning he complained of feeling unwell. Some time after, a physician was summoned, but when he arrived, it was too late to counteract the effects of the deadly poison, and the little sufferer died in great pain."

A Comprehensive Medical Dictionary: Containing the Pronunciation, Etymology and Signification of the terms made use of in Medicine and the Kindred Sciences, with an Appendix, comprising a list of all the more important articles of the Materia Medica arranged according to their medicinal properties. Also, an explanation of the Latin terms and phrases occurring in Anatomy, Pharmacy, &c.; together with the necessary directions for Writing Latin Prescriptions, &c. &c. By J. Thomas, M.D., &c. Philadelphia. J. B. Lippincott & Co. 1864. pp. 704.

In glancing over the title page of Dr. Thomas' Dictionary, one is struck with the extent of its grasp, and the valuable aid it promises to the student who may habitually consult its pages. Perhaps in no country will so great a diversity in the pronunciation of scientific terms be observed as in our own, where self-education is more common than in most others, and

University tuition less accessible. Our Medical and Pharmaceutical Institutions do not insist on preparatory classical studies, and the student is often found entering upon a professional career with an amount of preliminary education wholly inadequate to cope with the difficulties that beset him. To this numerous class, both as students and graduates, this work offers its aid; and, if its claims be at all commensurate with its promises, they will find it a constant helper on many needful occasions. Now, what does it promise? and how nearly does it come up to the mark? First, in regard to pronunciation. Dr. Thomas is the author of the system of pronunciation in "Lippincott's Gazetteer," and has given much attention to this important feature of the work. His plan, in most instances, divides the words into syllables by hyphens, and in this way, with accentuation marks, gives a good idea of the pronunciation intended; in others, a separate and distinct spelling, to represent the sounds of the word, is given, thus:—"Artemisia," is "Ar-te-mish'e-a;" "Chenopodiaceæ," is "Ke-no-po-de-á-she-é;" "Discutient," is "Dis-kú-shent."

The etymology of words derived from the French, Latin and Greek is very generally traced, and affords a convenient reference for writers and investigators. Besides the proper words employed in scientific nomenclature and terminology, an immense number of adjectives explanatory of the sciences are introduced and defined; more especially those used in medicine, pharmacy and botany. The pharmaceutical student will be particularly gratified and benefited by the light it sheds on his scientific pathway. The natural orders of plants are all given and defined, and also most articles of the materia medica.

In the Appendix, the explanation of Latin terms and phrases will meet a want felt in every apothecary's shop and physician's office, and the tabular statements of Latin names and adjectives there grouped, with especial reference to medicine and pharmacy, exhibit a happy familiarity on the part of the author with these wants.

In this part will also be found a useful "table of materia medica," arranged according to the therapeutic qualities of the drugs; and also a table of doses, both of which address themselves specially to the medical student.

The chapter on writing prescriptions may be studied by medical students with much advantage, and attention to the precepts it inculcates, by many physicians, would render these often obscure and hieroglyphic documents clear and easily understood. Of course the remarks bear more on the language than the composition of prescriptions, and do not embrace the numerous hints necessary to caution against chemical incompatibility or pharmaceutical impropriety, which a complete treatise on this branch of medical education would include.

The author, at the conclusion, gives a chapter of words, the pronunciation of which is disputed, with the several authorities for the variations.

In thus presenting some of the merits of Dr. Thomas's book, we heartily recommend it as a valuable handbook and lexicon, for constant reference by the physician and pharmaceutist.

In the course of our examination we have met with a few omissions and errors, which are difficult to avoid in a first edition of such a work. In several instances reference is made to other words which have not been introduced: thus, Abrotanum mas, is referred to Artemisia Abrotanum; Black Drop is referred to Opii Acetum; Abscissa vox is referred for definition to Vox abscissa; Acaweria to Ophioxylum; Alcargen to Cacodylic acid,—none of which are to be found. The definition of the term "*Liquor*" is not pharmacopœially correct, as, in their true signification, alcohol does not enter the "*Liquores*" of the U. S. Pharmacopœia. Goulard's Extract is defined Liquor Plumbi Diacetatus *dilutus*. Nicotina, the poisonous alkaloid of tobacco, is said to be "the same as Nicotianin," which last is described to be the odorous principle of tobacco. "Percolation" is not noticed as a pharmaceutical process equivalent to "displacement," and "dialysis," in its new chemical sense as a process nearly equivalent to *exosmosis*, has been overlooked.

These omissions and errors will doubtless be corrected in a future edition.

OBITUARIES.

Prof. Benjamin Silliman, of Yale College, died at his residence in the city of New Haven on the morning of Nov. 24, 1864, in the 86th year of his age. He was the son of General Gold S. Silliman, of a highly respectable Connecticut family, and was born in the town of Trumbull, Conn., in 1779; graduated at Yale College, 1796;—tutor in that institution 1799—1804, when he became Professor of Chemistry; in which station he continued until 1853, nearly fifty years, and then retired from the active duties of the Chair to become Emeritus Professor. In 1818 he founded the *American Journal of Science and Arts*, which he sustained alone for twenty years in the most liberal manner, at a great outlay of money, care and labor for a whole generation. Prof. Silliman was more widely known in Europe than any other American in the walks of science. "Amid all his engagements he forgot nothing, he neglected nothing, he was never in a hurry, and never shrank from duty. The whole working of his nature was so regulated and even, that it surprised no one to see him maintain himself unchanged at the age of four score." "In bodily presence and mental characteristics he was a perfect model of manhood. All his faculties were well balanced, and always in order for use. He was never taken by surprise, or thrown off his balance by any casualty. He was the most attractive lecturer in the country, from the amenity of his manner, the fluency of his diction, the clearness of his instruction, the aptness of his topics and the beauty of his experiments. When he entered upon his career, the science of chemistry had but just assumed its form, mineralogy was in a crude state as an appendix to chemistry, and geology was hardly thought of as a science. In the wonderful advances made since,

he has always kept himself abreast of the foremost in his intimate and accurate knowledge of every new discovery." "His position as the most widely known American, with his personal attractiveness, made his company and correspondence to be sought by many admirers in both hemispheres. Having a tolerable patrimony, he was able to exercise a liberal and graceful hospitality, and hundreds will remember the hours spent in his house as among the brightest oases of life."—*N. Y. Independent.*

Prof. Silliman mingled in the reunions of the last College commencement in July with his usual vivacity and amenity, but the last five years had told on the firmness of his step and his power of endurance. He was somewhat unwell a week or two before his decease, but awoke on the morning of his death, from a refreshing sleep, and soon after performing his usual morning devotion, he quickly asked his wife to raise his head, and was dead almost in an instant after. "Thus ended most fittingly a beautiful life. The model organism, so balanced in all its parts, and so true and regulated in its movements, had run its full time—and stopped."

Frederick L. John, one of the most able and successful pharmaceutists of Philadelphia, died on the 11th of December, 1864, in the fifty-fourth year of his age. Mr. John was born at Gehoven, in Prussia, on the 10th of April, 1811, and emigrated to this country in January, 1842. In 1844 he commenced business in Race street, on the site of his present establishment, and long before his decease had acquired a well deserved reputation as a practitioner of pharmacy. His application to business, in the earlier part of his career, was unremitting; especially was he devoted to the laboratory duties, which he superintended in person, and took great pride in having thoroughly done. Mr. John was regularly educated in Prussia as a pharmaceutist, and during his residence here cultivated an acquaintance with American botany. Among the medical profession, Mr. John had many friends, and stood deservedly high. He was a member of the Philadelphia College of Pharmacy and of the American Pharmaceutical Association, and sometimes attended the meetings. Mr. John was retiring and unassuming in his demeanor, possessed great integrity of character, and was charitable in his relations with the needy. Our intercourse with him has always been favorable to his excellence as a man, to his thoroughness as a pharmaceutist, and to his liberality as a votary of science.

Catalogue of the Class of the Philadelphia College of Pharmacy.

FOR THE FORTY-FOURTH SESSION, 1864–65.

With a List of their Preceptors and Localities.

MATRICULANTS.	TOWN OR COUNTY.	STATE.	PRECEPTOR.
Alise, Wm. E.	Philadelphia,	Pennsylvania,	Charles Ellis, Son & Co.
Austin, George	Terre Haute,	Indiana,	Thomas H. Barr.
Barnitz, Frank M.	York,	Pennsylvania,	W. B. Webb.
Bauer, Louis G.		Germany,	Oscar De Dobbeler.
Becker, G. H.	New Strelitz,	"	Of. Med. Direct. U. S. A.
Black, John, Jr.	Lancaster,	Pennsylvania,	C. A. Heinitsh.
Blair, Andrew	Philadelphia,	"	Andrew Blair.
Blair, Henry C.	"	"	Andrew Blair.
Braddock, Isaac A.	Haddonfield,	New Jersey,	C. S. Braddock.
Bomer, Augustus P.	Philadelphia,	Pennsylvania,	Wm. M. Reilly.
Brown, Samuel A.	"	"	J. R. Angney, M. D.
Brown, Thomas J.	Rockdale,	"	James T. Shinn.
Buchanan, Joseph Y.	Glasgow,	Scotland,	Andrew Blair.
Campbell, Hugh	Philadelphia,	Pennsylvania,	J. W. Simes, Jr.
Clarke, Thomas C., Jr.	"	"	Philadelphia Navy Yard.
Cornell, Edward A.	Williamsport,	"	Charles Ellis, Son & Co.
Cuthbert, Richard W.	Athensville,	"	O. S. Hubbell.
Day, Robert L.	Somerville,	New Jersey,	T. R. Coombe.
De Moll, Otto	Washington,	Dist. of Columbia,	C. F. Gristock.
De Young, Samuel H. S.	Philadelphia,	Pennsylvania,	Jos. Landschutz.
Ditman, Andrew J.	"	"	Peter Niskey.
Dobbins, Albert N.		New Jersey,	J. P. Thatcher.
Edwards, Wm. F.	Dover,	Delaware,	J. H. Kay.
Evans, J. Estell	May's Landing,	New Jersey,	French, Richards & Co.
Evans, Jonathan	Philadelphia,	Pennsylvania,	Charles Ellis, Son & Co.
Fergusson, John	Ary,	Scotland,	Powers & Weightman.
Furness, Thomas S.	Philadelphia,	Pennsylvania,	Ambrose Smith.
Gross, George A.	Harrisburg,	"	Thomas S. Wiegand.
Harry, J. W.	Conshohocken,	"	D. W. Harry.
Hays, Nathan W. C.	Burlington,	New Jersey,	Daniel S. Jones.
Heller, Marx M.	Cleveland,	Ohio,	Thomas J. Husband.
Hillary, John F.	Philadelphia,	Pennsylvania,	Wm. Hillary.
Huber, Milton	Norristown,	"	Wm. Stahler.
Johnson, Newton A.	Galesburg,	Illinois,	B. Smedley.
Jones, Samuel R.	Pittsburg,	Pennsylvania,	S. M. McCollin.
Keen, Francis	Philadelphia,	"	I. N. Marks.
Kennedy, Charles W.	"	"	Edmund Pollitt.
Kneeshaw, Wm. W.	Trenton,	New Jersey,	Hassard & Co.
Laird, Wm. R.	Reading,	Pennsylvania,	A. B. Taylor.
Loughlin, James	Philadelphia,	"	Edward Parrish.
Leeds, J. Elwood	"	"	Jenks & Middleton.
Levering, P. Wharton	Roxborough,	"	O. S. Hubbel.
Lindsay, J. B.	Philadelphia,	"	F. Brown.
Lippincott, Robert C.	"	"	R. Shoemaker & Co.
Little, Arthur H.	"	"	Bullock and Crenshaw.
McClure, Francis	Harrisburg,	"	John Reakirt.
McElroy, James B.	Philadelphia,	"	G. Krauss.

McPike, Wm. C.	Alton,	Illinois,	W. A. Holton & Co.
Mein, Bernard V.	Philadelphia,	Pennsylvania,	T. Morris Perot.
Meyer, John P.	Pottsville,	"	Joseph A. Heintzleman.
Millemann, Philip	Chicago,	Illinois,	Charles H. Eggert.
Miller, Abraham M.	Philadelphia,	Pennsylvania,	Thomas S. Wiegand.
Milliac, John	"	"	W. Patterson, M. D.
Moore, Charles C.	"	"	Bullock & Crenshaw.
Morell, Elijah S.	"	"	Charles Morell.
Moser, Americus H.	Allentown,	"	E. B. Garrigues.
Newbold, Henry A.	Philadelphia,	"	Powers & weightman.
Newbold, Thomas M.	"	"	French, Richards & Co.
Newton, John S.	"	"	Ralph Newton.
Nordell, Augustus	Rock Island,	Illinois,	Daniel Hershey, M. D.
Notson, Charles B.	Philadelphia,	Pennsylvania,	Wm. Notson, M. D.
Orth, Frederick C.	Hummelstown,	"	Philip Leidy.
Painter, Emlen	Delaware Co.,	"	Charles Shivers.
Pragheimer, A. E.	Philadelphia,	"	H. O. D. Banks & Co.
Parrish, Clemmons	"	"	Edward Parrish.
Pile, Gustavus	"	"	Wilson H. Pile, M. D.
Preston, David	Harford Co.,	Maryland,	Wm. Procter, Jr.
Price, J. M.	Philadelphia,	Pennsylvania,	C. Fronefield, M. D.
Price, Warren D.	"	"	Thomas Lancaster.
Ranck, J. W.	"	"	N. Ranck, M. D.
Rau, Robert	Bethlehem,	"	J. M. Maris.
Reakirt, Tryon	Philadelphia,	"	John Reakirt.
Remington, Joseph P.	"	"	Charles Ellis, Son & Co.
Riley, Charles W.	"	"	George A. Miller.
Rinker, Wm. H.	Roxborough,	"	John Moffet.
Robinson, Joshua K.	Newark,	Delaware,	O. S. Hubbell.
Ross, H. H.	Chester,	Pennsylvania,	M. Marshall, M. D.
Rubincam, Charles E.	Philadelphia,	"	Jenks & Middleton.
Rutherford, Charles	"	"	David Jameson.
Sayre, Lucius E.	Bridgeton,	New Jersey,	W. Opdyke, M. D.
Segner, William	Palmyra,	Pennsylvania,	J. P. Fetter, M. D.
Senderling, Charles	Philadelphia,	"	Joseph L. Shoemaker.
Shoemaker, Allen	"	"	R. Shoemaker & Co.
Shoemaker, B., Jr.	"	"	R. Shoemaker & Co.
Shoemaker, Charles	"	"	Edward Parrish.
Shoemaker, Wm. H.	Muncy,	"	Hassard & Co.
Simson, W. H.	Halifax,	Nova Scotia,	George Y. Shoemaker.
Smith, Wilson B.	Philadelphia,	Pennsylvania,	W. H. H. Githens.
Stadelman, S. F.	"	"	George Ashmead.
Stolte, Max Joseph	"	"	A. B. Taylor.
Strehl, Louis	Chicago,	Illinois,	John Bley.
Souder, Joseph A.	Philadelphia,	Pennsylvania,	W. R. Warner.
Taylor, James	"	"	James L. Bispham.
Van Orsdel, Wm. E.	N. Wilmington,	"	W. E. Van Orsdel.
Vogelbach, Edmund	Philadelphia,	"	Michael Kreitzer, M. D.
Walker, John Thomas	"	"	Jn. M. Pleis, Jr.
Walker, Thomas A.		New Jersey,	Robert C. Davis.
Webb, Samuel		Pennsylvania,	Elliot, White & Co.
Weber, Frank	Philadelphia,	"	J. Weber, M. D.
Weichselbaum, Jacob	"	"	Smith & Shoemaker.
Wendell, Edward	"	"	John G. Baker.
Wendell, Frederick	"	"	John Wendell, Jr.
White, James	"	"	Wyeth & Bro.
Williamson, Forest P.	Delaware Co.,	"	A. H. Yarnall.